POLYCYCLIC PEROXIDES AND PLANAR NITROGENS

Thesis by

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It's a mystery to me--the game commences
For the usual fee--plus expenses
Confidential information--it's in a diary
This is my investigation--it's not a public inquiry

I go checking out the reports--digging up the dirt
You get to meet all sorts in this line of work
Treachery and treason--there's always an excuse for it
And when I find a reason I still can't get used to it

And what have you got at the end of the day?
What have you got to take away?
A bottle of whiskey and a new set of lies
Blinds on the window and a pain behind the eyes

Scarred for life--no compensation
Private investigation

--Mark Knopfler

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As has been told a thousand times before, there are too many people I'm indebted to to ever have any hope of thanking all of them here. I'll try to cover the most important (or perhaps the most pertinent) ones here, and my sincerest apologies to those many deserving souls who have been omitted.

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Man cannot live on research alone, and I would like to thank all of the people who have made this other 10% of the

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Last but by no means least, I would like to thank my parents, who have spent endless time and money putting me through Caltech. I could not have made it through college without their support, monetary and otherwise.

ABSTRACT

1,6-diaza-3,4,8,9,12,13-hexaoxabicyclo[4.4.4] tetradecane (hexamethylene triperoxide diamine or HMTD) was found, by a single crystal x-ray study, to have planar bridgehead nitrogen atoms. In order to study this planarity, a synthesis was developed for HMTD analogs. Crystals structures were obtained for three of these analogs, 1,6-diaza-3,4,8,9-tetraoxabenzo-tricyclo[4.4.2]dodec-11-ene (benzene tetramethylene diperoxide diamine or BTDD), 1,8-diaza-10,11,14,15-tetraoxatricyclo[6.4.4.$0^{2,7}$]hexadecane (cyclohexyl tetramethylene diperoxide diamine or CTDD), and 1,6-diaza-3,4,8,9-hexaoxabicyclo[4.4.2]dodecane (hexamethylene diperoxide diamine or HMDD). These structures show that the planarity at the bridgehead nitrogen atoms of HMTD is no coincidence. MM2, a molecular mechanics program, was used to show that this planarity is not expected from simple force considerations. MNDO was used to model the molecule considering molecular orbitals. Finally, nuclear magnetic resonance techniques were used to obtain the energy of activation for inversion of HMTD and to determine the nuclear quadrupole coupling constants of the bridgehead nitrogen atoms at different temperatures, and thus their relative planarity.

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CHAPTER I. INTRODUCTION

Medium-ring bicyclic compounds are of great interest to chemists at the present time. These substances are ideal for studying the effects of severe strain upon organic molecules, especially the configurations which these molecules will adopt. This thesis presents the results of experiments on a rare subclass of medium-ring bicyclic molecules: those with several peroxide groups in the bridges and nitrogen atoms in the bridgeheads.

The only one of the compounds discussed in this thesis that has been known for a long time is HMTD. Before the experiments reported in this thesis were performed, there had been no serious attempt to obtain information pertaining to the structure of HMTD (with the sole exception of one NMR spectrum; see Chapter II). Since few crystal structures have been obtained for medium ring bicyclic compounds (their conformations have been studied using computers, for the most part), doing a crystal structure of HMTD was an attractive idea. On the basis of the interesting results of this experiment (that the bridgehead nitrogen atoms were planar), and the fact the these results were poorly understood, a synthesis was developed for similar compounds. Three of these compounds were made (BTDD, CTDD, and HMDD), and a crystal structure was solved for each.

These crystal structures confirmed the fact that the preferred angle between peroxide containing bridges as measured at the bridgehead nitrogen atoms is 120°. Furthermore, the trend

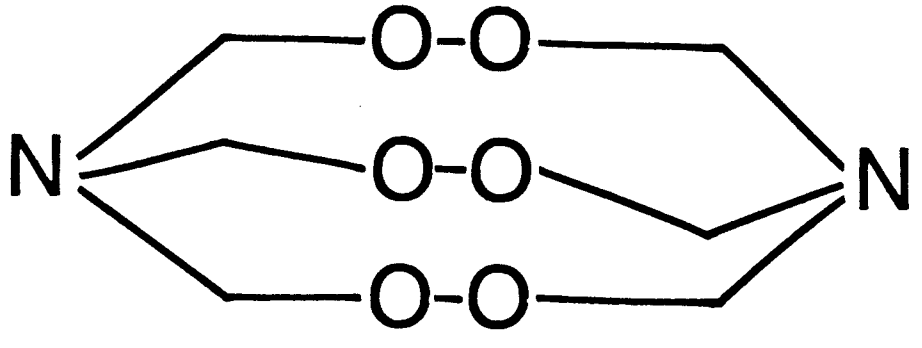
of short bond lengths, first seen in HMTD, continued in each of these molecules. At this point, it seemed appropriate to further investigate the effects that cause the planar nitrogen phenomenon. Computers were used to predict the structure of HMTD both classically and with semi-quantitative molecular orbital theory (in order to study electronic effects). These calculations suggested that both steric and electronic effects play a part in determining the structure of HMTD.

Once the static, solid state structure of these molecules had been determined, an obvious problem to tackle was the conformation of HMTD in solution. A proton NMR study was undertaken to determine the rate constant for ring flipping in HMTD, which could be expected to provide information concerning its conformation in solution. This process was in fact found to have two rate constants, which suggested that HMTD adopts different conformations at different temperatures in solution. Finally, a ^{14}N linewidth study was performed in order to get information about the relative planarity of the bridgehead nitrogen atoms at different temperatures, and to see how well this information was correlated with the proton NMR results. The bridgehead nitrogen atoms were found to be planar at low temperature and to move away from planarity at a higher temperature, with the same sharp break in slope seen in the proton experiments.

CHAPTER II. HMTD

A. Introduction

1,6-diaza-3,4,8,9,12,13-hexaoxabicyclo[4.4.4]tetradecane (hexamethylene triperoxide diamine or HMTD; see Figure II-1) was first synthesized in 1885 by Legler[1]. It was soon found to be a powerful initiating explosive and as such it was studied by Taylor and Rinkenbach of the Bureau of Mines[2]. Although it is inexpensive, easy to synthesize, relatively insensitive to shock (it requires a 3-cm drop of a 2-kg weight to detonate it, as compared to 0.25 cm for mercury fulminate), and more powerful than most initiating explosives, HMTD slowly decomposes when stored and so is not now of any commercial or military importance. HMTD has gone largely unnoticed since this study.



HMTD

HMTD.

Figure II-1

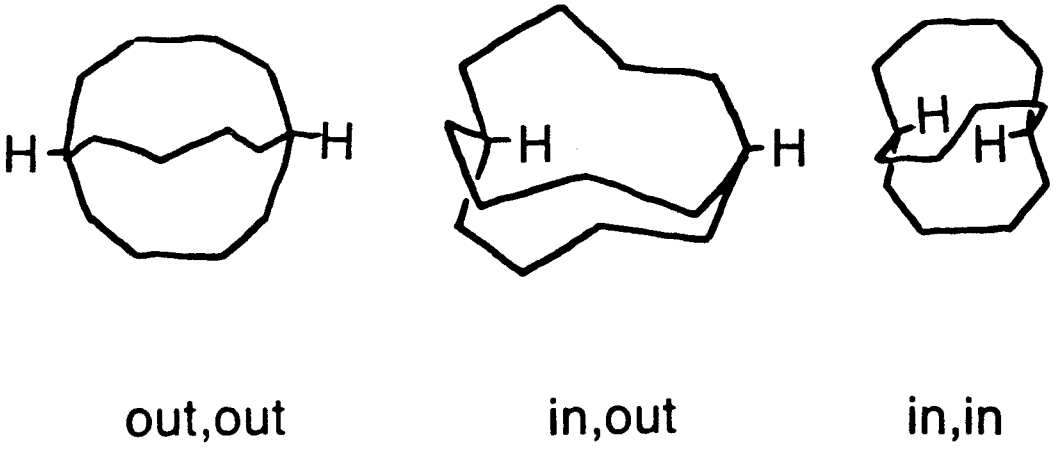
HMTD belongs to the group of compounds known as medium ring bicyclic compounds: bicyclic systems containing only 8-11 membered rings. There are only 10 possible basic skeletons for such compounds--[3.3.3], [4.4.2], [4.3.3], [5.4.2], [5.3.3], [4.3.3], [6.3.3], [5.4.3], [4.4.4], and [5.4.4]. There are three properties which make medium ring bicyclic compounds especially interesting: (1) high strain and unusual structures; (2) inside-outside isomerism; and (3) encapsulation of small species such as H^+.[3]

Creating a new bridge in an already strained medium ring monocycle is perhaps the most strain-enhancing trick one could play on it. For example, the strain energy per carbon atom in cyclodecane is 5 kJ mol^{-1}[4] and the average C-C-C bond angle is 116.7°[5] . If a four-member bridge is added to form the out,out isomer of bicyclo[4.4.4]tetradecane, the strain per carbon atom leaps up to 17 kJ mol^{-1} and the average C-C-C bond angle becomes 119° [3].

Another interesting facet of strain in these systems is that any process which allows outwardly pyramidalized bridgehead atoms to move toward planarity or pyramidalize inward brings considerable relief of strain. For example, 1-chlorobicyclo[3.3.3]undecane solvolyzes about 10^4 times faster than t-BuCl in aqueous alcohol, corresponding to the relief of 28 kJ mol^{-1} of strain energy, while 1-chlorobicyclo[4.4.4]tetradecane, it has been estimated, will solvolyze about 10^7 times faster than the t-BuCl, for a relief of 62 kJ mol^{-1} of strain.[6]

Inside-outside isomerism refers to the orientation of the

bridgehead atoms with respect to the central cavity of the molecule. A molecule in which both of the bridgehead atoms point into the cavity is termed in,in. If both of the bridgehead atoms point away from the cavity, the molecule is termed out,out, and if one bridgehead points inward and one outward the molecule is termed in,out Figure II-2). The bridgehead isomerism plays an important role in determining the strain of the molecule. A case in point is bicyclo[4.4.4]tetradecane. The out,out isomer of this molecule has a ΔH_f of -41 kJ mol^{-1}, whereas the in,out isomer has a ΔH_f of -91 kJ mol^{-1} and the in,in isomer has a ΔH_f of -32 kJ mol^{-1} (which is only slightly worse than the out,out isomer despite close hydrogen contacts).[3]



Possible nitrogen bridgehead conformations for bicyclic molecules.

Figure II-2

A question of great interest to many chemists is the identity of the smallest system that can encapsulate a proton, the smallest ion. Many medium ring bicyclic compound studies have been aimed at solving this question[7,8,9,10,11,12]. The smallest known encapsulating agent to date is 1,6-diazabicyclo[4.4.4] tetradecane[9], the "carbon analog" of HMTD. The fact that these two systems are almost equal in size suggests that HMTD also might be able to encapsulate protons. The conditions under which the carbon analog can be protonated, however, are too strenuous to use with HMTD.

Another great problem in the study of medium ring bicyclic compounds is the relative difficulty of their synthesis. It is clearly rather unfavorable thermodynamically to create such strained systems, and reaction sequences must be carefully designed to allow no alternate pathways[3]. In general, medium ring bicyclic compounds are generated in vigorous, relatively low-yield reactions. The synthesis for HMTD, on the other hand, is quite facile[13], which raised questions as to the proposed structure[14]. Although the structure was investigated by means of infrared spectroscopy[15], no conclusive structural evidence was presented until Urbanski took a proton NMR spectrum showing a singlet at a chemical shift of 4.83 parts per million[16]. X-ray crystallography seemed the perfect tool to further investigate this question.

B. Experimental

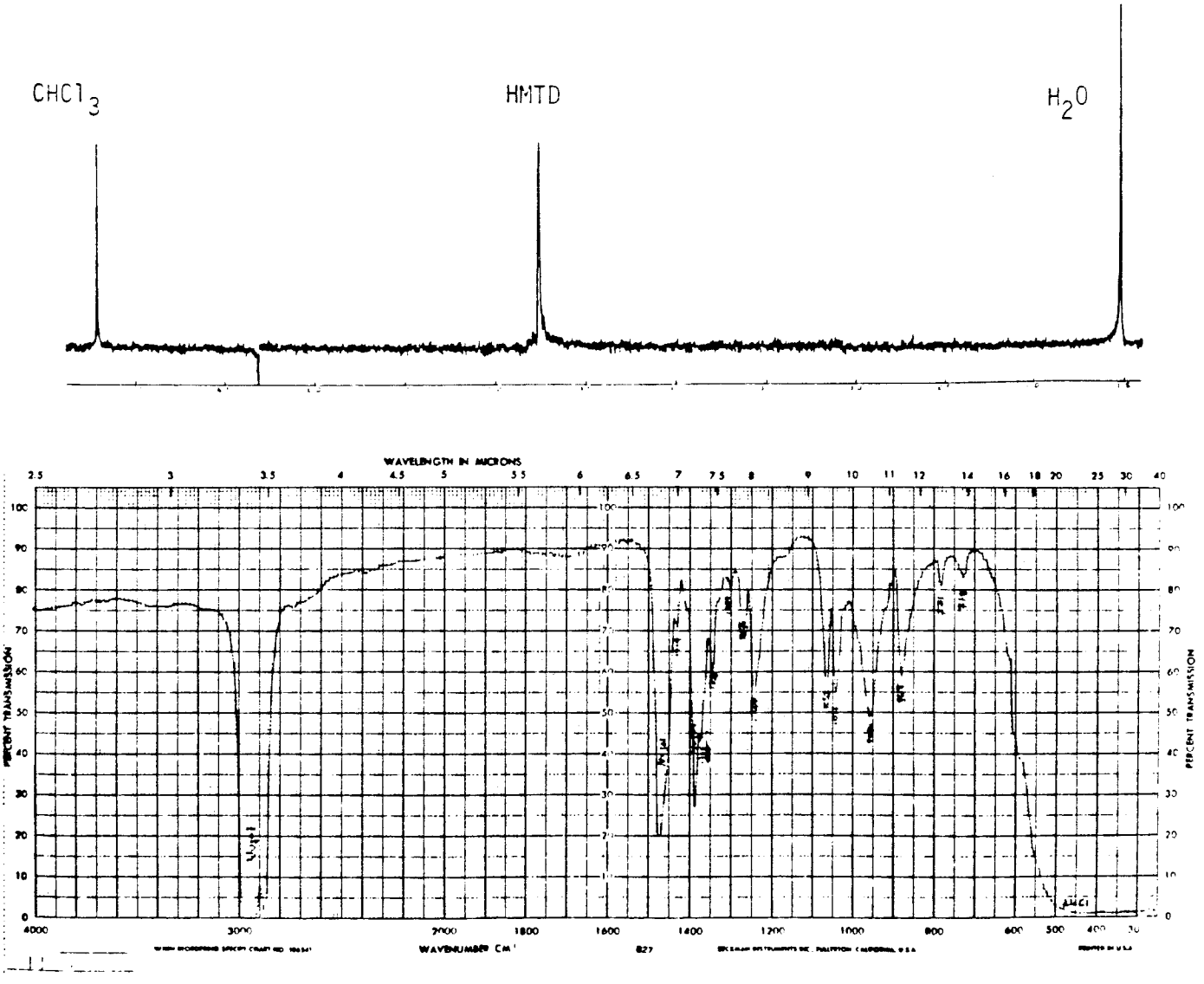
Fourteen grams of hexamethylenetetramine (HMTA) is dissolved in 45 g of 30% hydrogen peroxide and stirred mechanically at 0°C. Twenty-one grams of powdered citric acid is slowly added while the stirring continues. The mixture is stirred for three hours at 0°C and then is allowed to warm to room temperature and stand for two hours. The white crystalline product is filtered off, washed thoroughly with water, rinsed with methanol, and air dried. Yield is 50-70%. If larger portions are made (greater than double the recommended amount), the product will decompose exothermally while the solution warms. The product may be recrystallized from amyl acetate. HMTD may be stored under water with no risk of explosion and no increase in the rate of decomposition.

An elemental analysis of the product showed the following percentage composition:

Element	Expected %	Observed %
C	34.62	34.67
H	5.81	5.88
N	13.46	13.40

A proton nuclear magnetic resonance spectrum was taken at 500 MHz on a Bruker WM-500 machine. The spectrum showed a single peak at a chemical shift of 4.8 parts per million, in agreement with Urbanski's experiment[16]. There was little evidence of the

peak being anything other than a singlet. In addition, an infrared spectrum was taken showing peaks at 1419cm^{-1}, 1365cm^{-1}, 1335cm^{-1}, 1289cm^{-1}, 1257cm^{-1}, 1234cm^{-1}, 1053cm^{-1}, 1031cm^{-1}, 947cm^{-1}, 868cm^{-1}, 771cm^{-1}, and 718cm^{-1} (Figure II-3).



Proton NMR and IR Spectra of HMTD.

Figure II-3

A crystal (0.16 x 0.19 x 0.21 mm) that appeared satisfactory from oscillation photographs was centered on a CAD-4 diffractometer and a rhombohedral cell was found (Table II-1). Unit cell dimensions were calculated from the setting angles of 25 strong reflections with $22^\circ<2\theta$ (Mo Kα)$<36^\circ$. Data were collected with graphite-monochromated Mo Kα radiation (λ=0.71073A), θ-2θ scans, $2^\circ min^{-1}$ in 2θ for all $\pm h$, $\pm k$, $\pm l$ with $2\theta<50^\circ$, giving 1620 reflections. $(\sin\theta/\lambda)_{max}$ was 0.59. Backgrounds were measured for each reflection at the end of each scan, and the average background as a function of 2θ was calculated and used to correct measured scan counts. Three high-intensity reflections were monitored every 10,000 seconds for decay. A linear decay correction was applied, amounting to a total crystal decay of 8.6% over the time of the experiment. The possible space groups (no systematic absences) were *R*32, *R*3*m*, and *R*$\bar{3}$*m*. The structure was solved by Patterson and structure factor-Fourier techniques using the programs of the CRYM system[17] (form factors from International Tables for X-ray Crystallography[18]) minimizing $\Sigma w(F_o^2-F_c^2)^2$. No absorption correction was applied, since μr_{max} was 0.03. There were 155 unique reflections. The goodness-of-fit for the merging of this data was 1.99 ($S_{int}=(\Sigma w(F_o^2-\bar{F}_o^2)^2/(n-1))^{1/2}$) The nitrogen atoms were located from a Patterson map. Attempts to find an ordered solution in space group *R*32 failed, but a model in *R*3*m* refined to a final *R* index of 0.034 ($R=\Sigma||F_o|-|F_c||/\Sigma F_o$) and a goodness-of-fit of 2.84 ($S=[\Sigma w(F_o^2-F_c^2)^2/(n-p)]^{1/2}$,

Table II-1

Crystal Data for Hexamethylenetriperoxidediamine

$C_6H_{12}N_2O_6$

$N(CH_2O_2CH_2)_3N$

M_r=208.17

Space group *R3m* No. 160

Trigonal cell	Rhombohedral cell
a=10.417(5)Å	a=6.448(3)Å
c=6.975(3)Å	α=107.76(3)°
V=655.5(12)Å^3	V=218.5(4)Å^3
Z=3	Z=1

$F(000)$=330e

D_m=1.57 g cm^{-3} (ref. 2)

D_x=1.58 g cm^{-3}

Mo Kα, λ=0.71973Å

μ(Mo Kα)=1.53 cm^{-1}

μr_{max}=0.03

T=21°C

where n= number of independent reflections=155 and p=number of parameters=39). Individual reflections were assigned a weight w based on counting statistics plus a factor $(0.014I)^2$ to account for errors proportional to intensity (0.014 chosen by considering duplicate measurements). The weights of merged reflections were obtained by standard propagation of error plus an additional term, $(0.014\bar{I})^2$, to account for instrumental and other errors. $(\Delta/\sigma)_{max}$ was 0.0. The molecule was positioned with the two nitrogen atoms on a 3-fold axis and one carbon atom on a mirror plane. The other carbon atom and the two oxygen atoms are disordered across this mirror plane. All six atoms were refined with anisotropic thermal parameters. The four hydrogen atoms were introduced at calculated positions 0.95Å from the carbon atoms; they were repositioned twice, but their positions and assigned isotropic thermal parameters were never refined. These hydrogen positions suggest that the proton NMR spectrum ought to show an AB pattern, implying that in solution at room temperature the two chiral forms of HMTD interconvert rapidly to converge the signal into one singlet peak.

C. Structural Results and Discussion

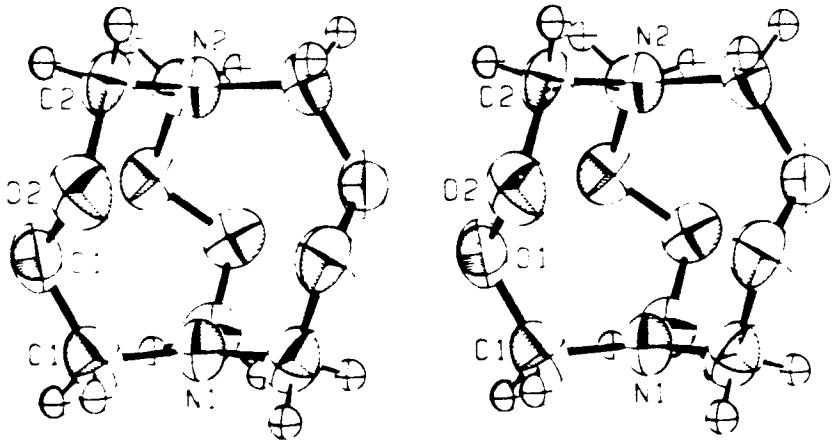
The most important finding of this x-ray study is that the bridgehead nitrogen atoms cannot be described as "in" or "out": each is planar within experimental error. The possibility that the planar geometry observed was the result of the nitrogen atoms being disordered between the in and out conformations was considered, even though the anisotropic thermal parameters did not support such a model. Isotropic half-nitrogen atoms were placed on either side of the carbon atom planes and the entire structure was refined again; at convergence the half-nitrogens were only 0.26(3)Å [N(1)] and 0.30(3)A [N(2)] apart or about 0.15Å from the carbon plane. This is the maximum separation expected based on the anisotropic thermal parameters, so one must conclude that the appropriate model is the one with single nitrogen atoms and a planar arrangement of carbon atoms about each of them.

The bond lengths and angles in the molecule are also of interest. The nitrogen-carbon bond lengths average 1.421(8)Å, indicative of an sp^2 hybridization at the nitrogen atoms. The carbon-oxygen bond lengths average 1.421(9)Å, a bit shorter than the 1.432Å one would expect based upon the structures of other organic peroxides[19,20,21,22,23,24,25,26,27,28,29]. The peroxide bond lengths are also short at 1.456(8)Å (as compared to the 1.479Å expected from the same structures). The carbon-oxygen-oxygen bond angles average 106.3(5)°, slightly smaller than the 107.8 expected from these studies. The peroxide torsion angle is 129.3(5)°; although this angle is 29° larger than expected in the

absence of other effects, it takes little energy to open this angle[30,31].

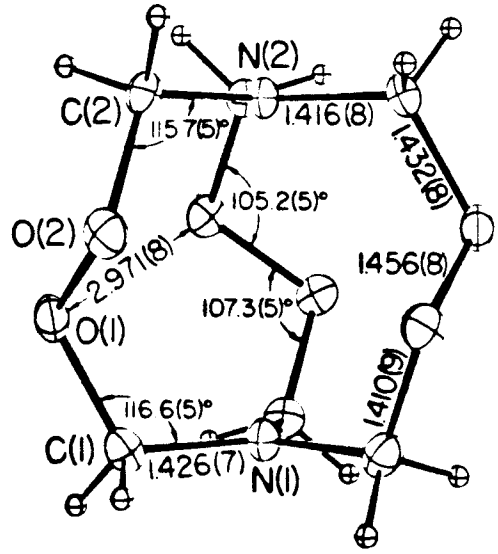
Final parameters are given in Table II-2, Bond lengths and angles in Table II-3, anisotropic thermal parameters in Table II-4, hydrogen positions in Table II-5, and structure factors in Table II-6. A stereoview of HMTD drawn with ORTEP[32] is presented in Figure II-4; Figure II-5 shows some important distances and angles.

A few other compounds exist with planar or nearly planar nitrogen atoms (the "expected" out of plane distance, if trimethylamine is a representative compound, is 0.52Å[33]). Although the geometry of the carbon analog is similar to that of HMTD[11], the bridgehead nitrogen atoms can definitely be termed in,in. The nitrogen atoms in this molecule are 0.311(3)Å from the carbon plane and the carbon-nitrogen-carbon angles average 115.5(2)°. While these values are far from normal, the 120.0° angles in HMTD are even more unusual. Newkome[34] has prepared a macro-bicyclic cryptand with planar bridgehead nitrogens (Figure II-6). Unfortunately, however, this compound is not very similar to HMTD, which limits its usefulness in this investigation. Other compounds with in,out or out,out configurations or with the coordination about nitrogen approaching planarity are also known[3].



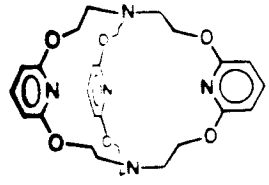
A stereoview of HMTD.

Figure II-4



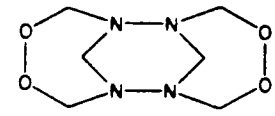
Important distances and angles.

Figure II-5



The macrobicyclic cryptand.

Figure II-6



The tricyclo tetradecane.

Figure II-7

An explanation for this unusual geometry may be sought in either steric or electronic factors. Table II-3 offers some insights into possible steric differences among HMTD, the carbon analog, Newkome's macrobicyclic cryptand, and a compound similar to HMTD, 1,2,7,8-tetraaza-4,5,10,11-tetraoxa-tricyclo[6.4.1.1^{2,7}]tetradecane[35] (henceforth called the "tricyclotetradecane"; see Figure II-7). If the explanation is steric, one might expect that the strain that forces the nitrogen atoms to be planar would evidence itself in other bond length or angle distortions. Bond lengths, where directly comparable, however, are shorter in HMTD than in the carbon analog[11], and they are everywhere shorter than in the relatively unconstrained tricyclotetradecane[35]. Moreover, the bond lengths in the crypt-and are all close to normal values, although space-filling models of this compound show why the planar geometry may be sterically favorable. The carbon-oxygen-oxygen angles in HMTD are normal,

whereas the carbon-carbon-carbon angles in the carbon analog are 7° larger than expected (and 10° larger than the HMTD angles). This may be rationalized partially in terms of qualitative molecular orbital models[36,37], which suggest that the lone pair-lone pair interactions between oxygen atoms in HMTD make enlarging the bond angle more difficult than do the methylene bond pair-bond pair interactions in the carbon analog. Models show that decreasing this angle moves the nitrogen atoms closer together, which should be energetically unfavorable. The nitrogen atoms of the carbon analog are much closer together than those of HMTD, however, an indication that it is not simply a nitrogen-nitrogen repulsion that determines the geometry about the nitrogen atom.

The largest difference between HMTD and the comparable compounds is found in the torsion angle about the peroxide bond (or the carbon-carbon-carbon-carbon torsion angle in the carbon analog). As mentioned above, this angle is 129°, 30° larger than expected in the absence of other effects. Closing this angle down from 129° forces the two nitrogen atoms together and also decreases the nonbonded O(1)···O(2) distance; both of these interactions are unfavorable. In HMTD there is an additional electrostatic repulsion between nitrogen atoms and oxygen atoms that is not present in the carbon analog, tending to keep the torsion angle large.

Electronic effects must represent some balance between the loss in energy caused by the sp^2 hybridization of the nitrogen atoms (rather than sp^3) and the gain obtained by shorter carbon-

nitrogen bonds. Since isolated C_3N systems are not planar, this balance must be net negative, but it is more than compensated for by other factors. Considering only the differences between the carbon analog and HMTD, any electronic effects are limited to those caused by a substitution of electronegative oxygen atoms for carbon atoms in the bridges. It is hard to imagine, however, just what type of electronic effects could make all of the bonds short. The anomeric effect could be invoked for shortening the nitrogen-carbon bonds (i.e., the nitrogen p orbital could be donating electron density to the low-lying carbon-oxygen σ^* orbital). This could do a lot as far as accounting for the observed geometry; the nitrogen atoms might planarize in order to achieve better overlap with the σ^* orbital. This argument is weak, however, in that the anomeric effect would be expected to lengthen the carbon-oxygen bonds, since electron density would be pumped into an antibonding orbital. Furthermore, it is difficult to imagine just what type of electronic effect could cause the shortening of the peroxide bond, since any effect that works on one oxygen atom must work on the other. If electron density is being pumped into each of the oxygen atoms, they should take on a partial negative charge and repel each other, lengthening the bond. There is a slightly better case for the withdrawal of electron density, in that making the oxygen lone pairs "smaller" might allow the atoms to move closer together to achieve better overlap despite their electrostatic repulsion. Oxygen being the most electronegative atom in the molecule, however, the withdrawal of electron density would seem rather unlikely. Fur-

thermore, the nitrogen-carbon bond lengths are extremely short, rendering this explanation unlikely also.

It seems from these considerations that neither steric nor electronic effects can entirely explain the observed effects. Thus, three major points need to be addressed: (1) Is the unusual geometry of HMTD simply coincidental? (2) What role do steric effects play in this geometry? and (3) What role do electronic effects play in this geometry?

Table II-3

Final Heavy-Atom Parameters for HMTD

atom	x	y	z	U_{eq}[a]	POP[b]
N(1)	0	0	-0.2309	0.0410(10)	3.0
C(1)	0.1156(6)	0.1512(7)	-0.2301(11)	0.0518(16)	9.0
O(1)	0.1864(4)	0.2090(4)	-0.0531(10)	0.0525(11)	9.0
O(2)	0.0829(5)	0.2281(4)	0.0673(11)	0.0511(12)	9.0
C(2)	0.0785(2)	$-x$	0.2448(8)	0.0420(8)	9.0
N(2)	0	0	0.2413(10)	0.0337(9)	3.0

a. $U_{eq}=1/3\Sigma_i \Sigma_j[U_{ij}(a_i^* a_j^*)a_i \cdot a_j]$ $\sigma U_{eq}=(1/6^{1/2})<\sigma U_{ii}/U_{ii}>U_{eq}$

b. The number of atoms in the unit cell.

Table II-3

Bond Distances (Å) and Angles in HMTD and Related Compounds

bond or angle	HMTD	carbon analog	tricyclo-tetradecane	cryptand
N(1)-C(1)	1.426(8)	1.443(3)	1.434(1)	1.442(2)
N(2)-C(2)	1.416(8)	1.443(3)	1.459(1)	
O(1)-O(2)	1.456(8)		1.472(1)	
C(1)-O(1)	1.432(8)	1.520(4) (C-C)	1.445(1)	
C(2)-O(2)	1.410(9)		1.428(1)	
C(1)-N(1)-C(1)	120.0(5)	115.5(2)		120.0(1)
C(2)-N(2)-C(2)	120.0(5)			
N(1)-C(1)-O(1)	116.6(5)	114.1(2) (N-C-C)	115.5(1)	112.8(1) (N-C-C)
C(1)-O(1)-O(2)	107.3(5)	116.4(2) (C-C-C)	106.0(1)	
O(1)-O(2)-C(2)	105.2(5)		109.2(1)	
O(2)-C(2)-N(2)	115.7(5)		111.5(1)	
N(1)-N(2)	3.193(7)	2.806(3)		
C(1)-O(1)-O(2)-C(2)	129.3(5)	90.1(2) (C-C-C-C)	100	

Table II-4

Anisotropic Thermal Parameters (x 10^4) for HMTD

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	359(20)	U_{11}	514(32)	$1/2U_{11}$	0	0
C(1)	508(39)	447(30)	550(43)	201(14)	77(24)	106(23)
O(1)	417(22)	390(23)	585(27)	65(21)	71(20)	4(19)
O(2)	597(47)	335(18)	610(21)	239(18)	29(23)	6(18)
C(2)	421(17)	U_{11}	482(25)	258(20)	-40(8)	$-U_{13}$
N(2)	268(17)	U_{11}	476(34)	$1/2U_{11}$	0	0

The form of the anisotropic thermal parameter is

$$\exp[-2\pi^2(U_{11}h^2a^{*2}+.....+2U_{23}klb^*c^*)]$$

Table II-5

Hydrogen Parameters for HMTD

Atom	x	y	z	B
H(1A)	0.0743	0.2096	-0.2719	4.0
H(1B)	0.1891	0.1606	-0.3187	4.0
H(2A)	0.1777	0.1888	0.2821	4.0
H(2B)	0.0331	0.1880	0.3379	4.0

Table II-6

Structure Factors for HMTD

The columns contain, in order, l, $10F_o$, $10F_c$, and $10\{(F_o^2-F_c^2)/\sigma(F_o^2)\}$.

0 0 L

3	289	272	57
6	338	323	40

0 1 L

2	479	495	-44
5	40	38	11
8	32	26	14

0 2 L

1	385	376	28
4	269	273	-17
7	54	47	28

0 3 L

3	133	131	10
6	123	128	-37

0 4 L

2	117	120	-31
5	110	108	8

0 5 L

1	221	220	4
4	235	236	-5
7	61	59	6

0 6 L

3	103	102	11
6	66	66	0

0 7 L

2	221	225	-21
5	-12	6	-9

0 8 L

1	146	144	17
4	113	113	3

0 9 L

3	47	48	-6

0 10 L

2	13	23	-14

1 0 L

1	629	650	-45
4	391	381	31
7	134	126	53

1 1 L

0	697	668	54
3	95	94	16
6	104	100	30

1 2 L

2	293	307	-63
5	116	111	38
8	51	44	33

1 3 L

1	238	239	-4
4	138	140	-17
7	49	51	-10

1 4 L

3	12	7	8
6	43	42	7

1 5 L

2	145	142	24
5	93	91	12

1 6 L

1	90	89	7
4	49	52	-23

1 7 L

3	36	32	19

1 8 L

2	65	68	-21
5	21	27	-12

1 9 L

1	19	19	1

2 0 L

2	620	645	-52
5	37	30	25
8	60	56	13

2 1 L

1	515	511	8
4	62	68	-51
7	36	42	-24

2 2 L

0	199	202	-18
3	121	118	26
6	28	31	-10

2 3 L

2	223	223	0
5	52	51	10

2 4 L

1	219	217	8
4	54	58	-24
7	44	47	-13

2 5 L

3	46	47	-9
6	35	36	-6

2 6 L

2	145	144	6
5	70	70	4

2 7 L

1	35	32	15
4	102	99	27

2 8 L

3	35	30	17

2 9 L

2	32	28	15

3 0 L

0	966	945	27
3	219	230	-62
6	129	132	-20

3 1 L

2	142	140	18
5	35	32	15

3 2 L

1	139	138	6
4	129	131	-19
7	23	20	6

3 3 L

0	295	279	66
3	125	127	-18
6	78	82	-27

3 4 L

2	229	229	0
5	90	92	-12

3 5 L

1	89	90	-13
4	156	156	-3

3 6 L

3	58	57	5

3 7 L

2	15	15	0

3 8 L

1	50	49	5

4 0 L

1	76	77	-10
4	67	63	21
7	62	60	8

4 1 L

0	378	350	96
3	154	155	-3
6	81	81	-3

4 2 L

2	103	100	24
5	69	69	2

4 3 L

1	65	67	-20
4	105	110	-46

4 4 L

0	121	119	14
3	109	111	-24
6	61	57	22

4 5 L

2	143	139	33
5	52	59	-35

4 6 L

1	87	88	-9
4	65	64	2

4 7 L

3	53	54	-5

5 0 L

2	460	458	5
5	52	58	-29

5 1 L

1	225	233	-49
4	108	111	-24
7	20	19	2

5 2 L

0	163	160	19
3	69	67	13
6	51	52	-4

5 3 L

2	290	295	-24
5	29	29	-3

5 4 L

1	49	49	0
4	122	122	0

5 5 L

0	167	162	30
3	101	99	25

5 6 L

2	24	24	1

5 7 L

1	15	12	6

6 0 L

0	188	181	44
3	123	122	8
6	54	49	22

6 1 L

2	142	145	-19
5	64	64	0

6 2 L

1	80	85	9
4	51	53	-11

6 3 L

0	125	125	5
3	75	77	-12

6 4 L

2	64	68	-26

6 5 L

1	36	32	16

6 6 L

0	12	5	5

7 0 L

1	35	30	17
4	68	73	-26

7 1 L

0	39	38	7
3	143	144	-5

7 2 L

2	147	146	4
5	17	8	15

7 3 L

1	20	18	4
4	45	46	-4

7 4 L

0	71	72	-1
3	68	65	14

8 0 L

HMID STRUCTURE FACTORS

2 188 192 -25
5 57 62 -20

8 1 L

1 66 69 -21
4 20 23 -6

8 2 L

0 87 89 -22
3 23 19 12

8 3 L

2 12 9 2

8 4 L

1 53 48 23

9 0 L

0 82 76 28
3 39 42 -13

9 1 L

2 37 23 50

9 2 L

1 40 38 7

10 0 L

1 93 87 33

10 1 L

0 25 32 -25

CHAPTER III. BTDD, CTDD, and HMDD

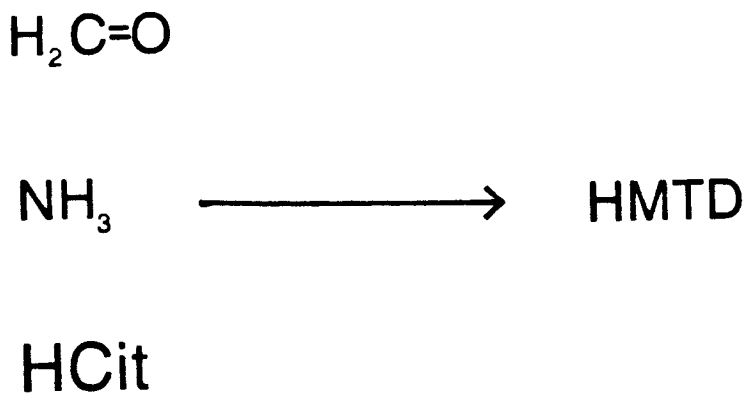
A. Introduction

Perhaps the most sensible way to investigate whether or not the geometry found in HMTD is accidental is to synthesize and study similar compounds. A few similar compounds had already been synthesized at the time the crystal structure of HMTD was completed: the tricyclotetradecane[35], a peroxide-containing urea adduct, and a similar ethylamine adduct[36]. The tricyclo tetradecane is the only one of these compounds which has been characterized; the other two exist as oils which decompose rapidly. Since these last two compounds are of little crystallographic use, a synthesis had to be developed in order to make new analogs.

The synthesis of HMTD, for all intents and purposes, makes use of only two substances: HMTA and hydrogen peroxide. HMTA, however, is simply an adduct of formaldehyde and ammonia (Figure III-1), suggesting that similar reactions may be run using other nitrogen-containing compounds. It is reasonable to assume that the mechanism of the HMTD reaction revolves around ammonia condensing with formaldehyde followed by a nucleophilic attack by peroxide. This is borne out by the synthesis of the tricyclotetradecane and the other adducts. In the former case the reagents are hydrazine, hydrogen peroxide, and formaldehyde; in the latter cases, the amines are reacted with hydrogen peroxide and formaldehyde. The only constraint on these reac-

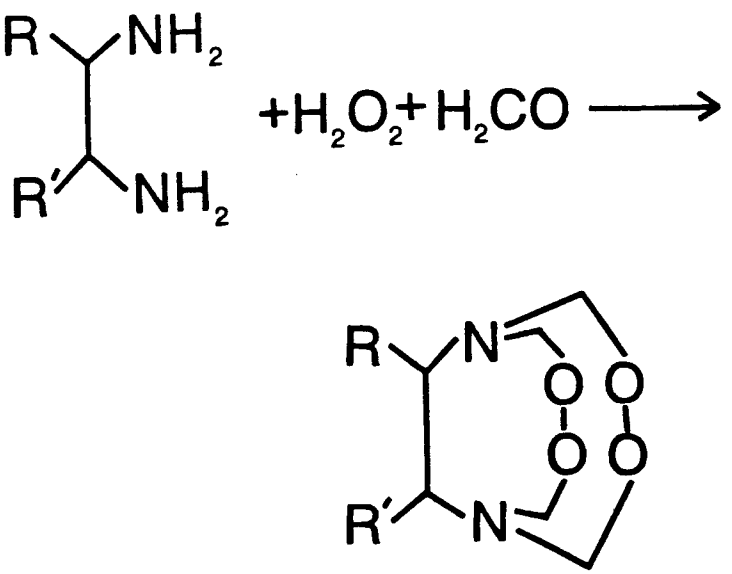
tions is that the reaction mixture not be too basic (which apparently catalyzes peroxide decomposition).

It thus seemed reasonable to attempt similar reactions on other amines. Monoamines are not of too much use in this problem, however, as it does not appear that they would react to produce polycyclic structures. The obvious class of compounds to try, then, was diamines. In particular, viscinal diamines seemed to be an appropriate starting point, as these compounds are easily obtained and the close proximity of the amine groups might make the reaction more favorable than in other cases (i.e., geminal diamines and 1,*n* diamines where *n* is greater than 2). Furthermore, space-filling models showed that the sought after structures were sterically reasonable (Figure III-2 shows the proposed reaction scheme). When the reaction was proven viable with ortho-phenylene-diamine, it was decided to synthesize a series of compounds with varying degrees of freedom of rotation in the two carbon bridge containing the two amine groups. The reaction indeed proved viable in all non-hindered viscinal diamines which were tested. Thus, crystal studies were done on the adducts of ortho-phenylene-diamine, 1,2-*trans*-diamino cyclohexane, and ethylene diamine, a series in which the bridge in question went from being utterly rigid to being more or less free to rotate.



A general reaction scheme for HMTD.

Figure III-1



Reaction scheme for viscinal diamines.

Figure III-2

B. Experimental

i. BTDD

45g H_2O_2 and 60ml formaldehyde solution (37%) are mixed and cooled to 0°C. One gram of ortho-phenylene-diamine is added, and the solution is stirred for one hour. The fine white crystals are collected and washed with ethanol. The compound may be recrystallized from amyl acetate.

An elemental analysis showed the following percentage composition:

Element	Expected %	Observed %
C	53.56	53.61
H	5.40	5.35
N	12.50	12.57

These data are consistent with those expected for 1,6-diaza-3,4,8,9-tetraoxabenzo-tricyclo[4.4.2]dodec-11-ene (which has been named benzene tetramethylene diperoxide diamine, or BTDD; see Figure III-3). The density, measured by flotation, was 1.46(3)g cm^{-3}.

An irregular crystal, 0.33 x 0.33 x 0.44mm that appeared satisfactory from oscillation photographs was centered on a CAD-4 diffractometer and an orthorhombic unit cell was found

Table III-1

Crystal Data for Benzene Tetramethylene Diperoxide Diamine

$C_{10}H_{12}N_2O_4$

M_r=224.22

Space group *Pbca* No. 61

Orthorhombic cell

a=7.635(1)Å

b=11.041(1)Å

c=24.249(2)Å

V=2044.1(6)Å^3

Z=8

$F(000)$=944e

D_m=1.46(3)g cm^{-3}

D_x=1.46g cm^{-3}

Mo Kα, λ=0.71073Å

μ(Mo Kα)=1.23cm^{-1}

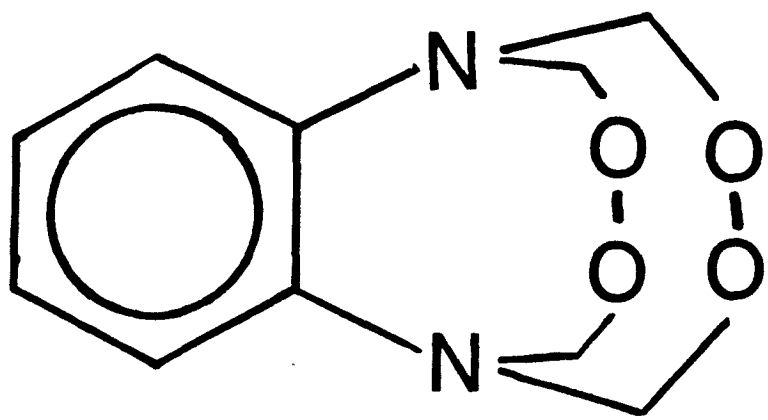
μr_{max}=0.039

T=21°C

(Table III-1). Unit cell dimensions were calculated from the setting angles of 25 strong reflections with $19<2\theta<21^{\circ}$ and refined by least squares. Data were collected with graphite-monochromated Mo Kα radiation (λ=0.71073Å), θ-2θ scans, $2^{\circ}min^{-1}$ in 2θ, with $4<2\theta<50^{\circ}$. $(\sin\theta/\lambda)_{max}$ was 0.59. Backgrounds were measured for each reflection at the end of each scan, and the average background as a function of 2θ was calculated and used to correct measured scan counts. 3950 reflections were collected in the $\pm$h, k, l octants (h -9 to 9, k 0 to 13, l 0 to 28). Three high-intensity reflections were monitored every 10,000 seconds for decay, showing a linear decay of 0.14%/hour (7.29% total) in F magnitudes. The systematic absences, 0kl, k odd, h0l, l odd, and hk0, h odd, and the unit cell dimensions indicated orthorhombic space group Pbca. 1785 unique reflections were used in the structure refinement with no reflections deleted. No absorption correction was applied, since μr_{max} was 0.039. The goodness-of-fit for the data merging (S_{int} is the RMS value of $(\Sigma w(F_o^2-\overline{F}_o^2)^2/(n-1))^{1/2}$) was 1.03. The structure was solved with MULTAN-78[39]. H atoms were placed at calculated positions and not refined (a 0.95Å bond length was used). 143 parameters were refined minimizing $\Sigma w(F_o^2-F_c^2)^2$ with the programs of the CRYM system[17] (form factors from International Tables for X-ray Crystallography [18]). The final R factor for $F_o>0$ ($R=\Sigma||F_o|-|F_c||/\Sigma F_o$) was 0.0707, and the final goodness-of-fit ($S=[\Sigma w(F_o^2-F_c^2)^2/(n-p)]^{1/2}$) was 2.97 (both from the final converged least squares fit). Individual reflections were assigned a weight w based on counting statistics plus a factor $(0.014I)^2$ to account for errors

proportional to intensity (0.014 chosen by considering duplicate measurements). The weights of merged reflections were obtained by standard propagation of error plus an additional term, $(0.014\bar{I})^2$, to account for instrumental and other errors. $(\Delta/\sigma)_{max}$ was 0.07. $(\Delta\rho)_{max}$ was 0.38e/Å^3 and $(\Delta\rho)_{min}$ was -0.52e/Å^3.

Oxygens 1 and 2 were disordered between two orientations with populations 0.835(8) and 1-0.835. Oxygens 3 and 4 were similarly disordered with populations 0.588(7) and 1-0.588.



Benzene Tetramethylene Diperoxide Diamine

Figure III-3

ii. CTDD

45g H_2O_2 and 60ml formaldehyde solution (37%) are mixed and cooled to 0°C. Two milliliters of *trans*-1,2-diaminocyclohexane is added, and the solution is stirred for one hour. The crystals are collected and washed with ethanol. Recrystallization is from amyl acetate.

An elemental analysis showed the following percentage composition:

Element	Expected %	Observed %
C	52.16	52.48
H	7.88	7.75
O	12.17	12.24

These data agree well with the expected percentages for 1,8-diaza-10,11,14,15-tetraoxatricyclo[6.4.4.$0^{2,7}$]hexadecane (which has been named cyclohexyl tetramethylene diperoxide diamine or CTDD; see Figure III-4). The density, measured by flotation, was 1.33(4)g cm^{-3}.

Two irregular crystals, 0.41 x 0.26 x 0.30 mm and 0.33 x 0.26 x 0.26 mm, were studied, due to decay problems. The crystals were coated with epoxy and oscillation photos were taken and appeared satisfactory. The crystals were each centered on a CAD-4 diffractometer, and a triclinic unit cell was found in each

Table III-2

Crystal Data for Cyclohexyl Tetramethylene Diperoxide Diamine

$C_{10}H_{18}N_2O_4$

M_r=230.26

Space group $P\bar{1}$ No. 2

Triclinic cell

a=6.948(1)Å

b=8.153(2)Å

c=11.124(2)Å

α=73.88(2)°

β=76.28(1)°

γ=68.97(2)°

V=559.3(4)Å^3

Z=2

$F(000)$=248e

D_m=1.33(4)g cm^{-3}

D_x=1.36g cm^{-3}

Mo Kα, λ=0.71073Å

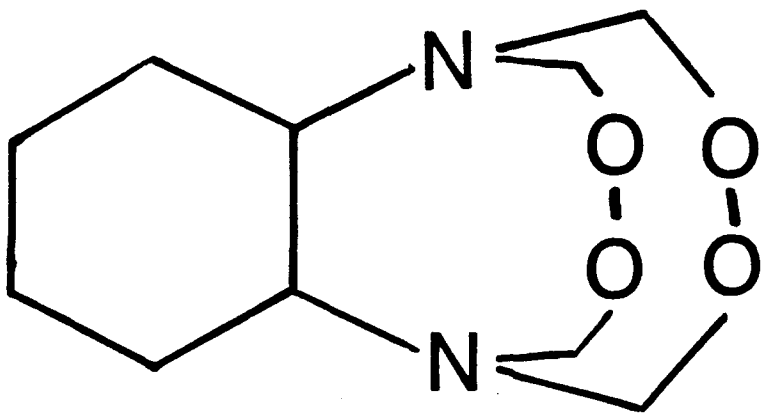
μ(Mo Kα)=1.13cm^{-1}

μr_{max}=0.032

T=21°C

case (Table III-2). Unit cell dimensions were calculated from the setting angles of 25 strong reflections (of each crystal) with $19<2\theta<21^{\circ}$. Each unit cell was refined by least squares, and the final cell dimensions were averaged. Data were collected with graphite-monochromated Mo Kα radiation (λ=0.71073Å), θ-2θ scans, 2° min^{-1} in 2θ, with $4<2\theta<50^{\circ}$. $(\sin\theta/\lambda)_{max}$ was 0.59. Backgrounds were measured for each reflection at the end of each scan, and the average background as a function of 2θ was calculated and used to correct measured scan counts. 2110 and 2113 reflections were collected in the +h, +k, l and +h, +k, -l hemispheres (h -8 to 8, k -9 to 9, l 0 to 13 and -13 to 0). Three high-intensity reflections were monitored for decay every 10,000 seconds, showing linear decays of 0.32%/hour (9.4% total) and 0.40%/hour (12.0% total) in F magnitudes. Two reflections were deleted and 1961 unique reflections were used in structure solution and refinement. No absorption correction was applied, as $\mu \cdot r_{max}$ was 0.032. The goodness-of-fit for the data merging (S_{int} is the RMS value of $(\Sigma w(F_o^2-\bar{F}_o^2)^2/(n-1))^{1/2}$) was 2.47. The structure was solved with MULTAN-78[38]. H atoms were placed at calculated positions and not refined (a 0.95Å bond length was used). 145 parameters were refined minimizing $\Sigma w(F_o^2-F_c^2)^2$ with the programs of the CRYM system[17] (form factors from <u>International Tables for X-ray Crystallography</u>[18]). The final R factor for $F_o>0$ ($R=\Sigma||F_o|-|F_c||/\Sigma F_o$) was 0.0732, and the final goodness-of-fit ($S=[\Sigma w(F_o^2-F_c^2)^2/(n-p)]^{1/2}$) was 3.60 (both from the final converged least squares fit). Individual reflections were assigned a weight w based on counting statistics plus a factor

$(0.014I)^2$ to account for errors proportional to intensity (0.014 chosen by considering duplicate measurements). The weights of merged reflections were obtained by standard propagation of error plus an additional term, $(0.014\bar{I})^2$, to account for instrumental and other errors. $(\Delta/\sigma)_{max}$ was 0.0. $(\Delta\rho)_{max}$ was 0.64e/Å^3 and $(\Delta\rho)_{min}$ was -0.38e/Å^3.



Cyclohexyl Tetramethylene Diperoxide Diamine

Figure III-4

iii. HMDD

45g H_2O_2 and 60ml formaldehyde solution (37%) are mixed and cooled to 0°C. Two milliliters of ethylenediamine is added, and the solution is stirred for one hour. The fine white crystals are collected and washed with ethanol. The compound may be recrystallized from amyl acetate.

An elemental analysis showed the following percentage composition:

Element	Expected %	Observed %
C	40.91	40.95
H	6.82	6.69
N	15.90	15.68

These data are consistent with those expected for 1,6-diaza-3,4,8,9-tetraoxabicyclo[4.4.2]dodecane (which has been named Hexamethylene diperoxide diamine, or HMDD; see Figure III-5). The density, measured by flotation, was 1.44(2)g cm^{-3}.

An irregular crystal 0.48 x 0.37 x 0.33 mm was mounted and coated with epoxy. An oscillation photograph appeared satisfactory, so the crystal was mounted on a CAD-4 diffractometer and a c-centered monoclinic cell was found (Table III-4). Unit cell dimensions were calculated from the setting angles of 25 strong reflections with $15<2\theta<25°$ and refined by least squares. Data

Table III-4

Crystal Data for Hexamethylene Diperoxide Diamine

$C_6H_{12}N_2O_4$

$M_r = 176.17$

Space Group C2/c No. 15

Monoclinic cell

$a = 11.937(1)$ Å

$b = 5.864(1)$ Å

$c = 11.890(1)$ Å

$\beta = 110.00(1)^\circ$

$V = 782.1(3)$ Å^3

$Z = 4$

$F(000) = 376e$

$D_m = 1.44(2)$ g cm^{-3}

$D_x = 1.50$g cm^{-3}

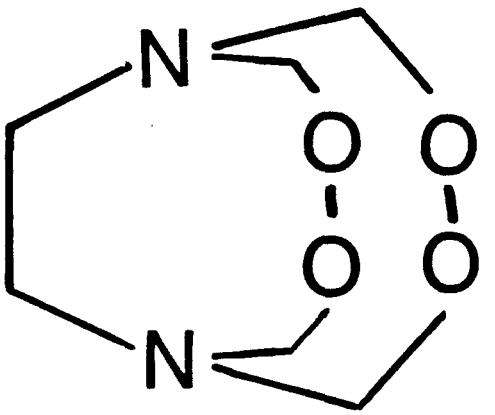
Mo Kα, $\lambda = 0.71973$Å

μ(Mo Kα) = 1.35cm^{-1}

$\mu r_{max} = 0.093$

$T = 21^\circ$C

Data were collected with graphite-monochromated Mo K radiation (λ=0.71073Å), θ-2θ scans, 2°min^{-1} in 2θ, with 4<2θ<50°. $(\sin\theta/\lambda)_{max}$ was 0.59. Backgrounds were measured for each reflection at the end of each scan, and the average background as a function of 2θ was calculated and used to correct measured scan counts. 2767 reflections were collected over an entire sphere with h -14 to 14, k -6 to 6, and l -14 to 14. Three high-intensity reflections were monitored every 10,000 seconds for decay, showing a linear decay of 7.5% in F magnitudes. The systematic absences, hkl, h + k odd, and h0l, l odd, indicated space group C2/c. 681 unique reflections were used in the structure refinement with no reflections deleted. No absorption correction



Hexamethylene Diperoxide Diamine

Figure III-5

was applied, since μr_{max} was 0.093. The goodness-of-fit for the data merging (S_{int} is the RMS value of $(\Sigma w(F_o^2-\bar{F}_o^2)^2/(n-1))^{1/2}$) was 1.15. The structure was solved with MULTAN-78[38]. The final R factor for $F_o>0$ ($R=\Sigma F_o - F_c / \Sigma F_o$) was 0.0305, and the final goodness-of-fit ($S=[\Sigma w(F_o^2-F_c^2)/(n-p)]^{1/2}$) was 3.79 (both from final converged least squares fit). Individual reflections were assigned a weight w based on counting statistics plus a factor $(0.014I)^2$ to account for errors proportional to intensity (0.014 chosen by considering duplicate measurements). The weights of merged reflections were obtained by standard propagation of error plus an additional term, $(0.014\bar{I})^2$, to account for instrumental and other errors. $(\Delta/\sigma)_{max}$ was 0.06. $(\Delta\rho)_{max}$ was 0.16 e/Å^3 and $(\Delta\rho)_{min}$ was -0.19 e/Å^3.

C. Structural Results and Discussion

Following are tables of data on BTDD, CTDD, and HMDD. Tables III-5 through III-10 relate to BTDD. These Tables contain, in order, final parameters, distances, angles, anisotropic thermal parameters, and structure factors. Tables III-11 through III-16 give the same information on CTDD, and Tables III-17 through III-21 give the same information for HMDD (except for hydrogen positions; the hydrogens in HMDD were refined, so these parameters will be found in Table III-15 rather than a separate Table). In addition, Table III-22 compares important distances and angles in HMTD, BTDD, CTDD, HMDD, and the tricyclo tetradecane.

Figure III-6 is an ORTEP[32] drawing of BTDD. Figure III-7 is an ORTEP drawing of CTDD. Finally, Figure III-8 is an ORTEP drawing of HMDD.

Table III-5

Atomic parameters for BTDD

(x,y,&z X 10^4; U and U_{eq} in $Å^2$ X 10^4)

atom	x	y	z	U or U_{eq}
C(1)	7955(3)	2485(2)	6098(1)	386(6)*
C(2)	9150(3)	1559(2)	5986(1)	383(6)*
C(3)	8882(4)	820(3)	5537(1)	484(7)*
C(4)	7442(5)	969(3)	5201(1)	577(8)*
C(5)	6249(4)	1866(3)	5315(1)	583(8)*
C(6)	6502(4)	2615(3)	5761(1)	497(7)*
C(7)	7778(4)	2868(3)	7093(1)	572(8)*
C(8)	9415(4)	4262(3)	6494(3)	572(8)*
C(9)	10344(4)	624(3)	6817(1)	520(7)*
C(10)	12141(4)	2084(3)	6287(1)	586(9)*
N(1)	8207(3)	3286(2)	6556(9)	426(5)*
N(2)	10614(3)	1358(2)	6341(9)	424(5)*
O(1A)	9053(3)	2124(3)	7363(1)	513(10)
O(1B)	7944(23)	1494(14)	7174(6)	708(62)
O(2A)	8824(3)	894(3)	7131(1)	499(10)
O(2B)	9671(24)	1475(15)	7302(6)	712(56)
O(3A)	11011(5)	4027(3)	6210(2)	541(15)
O(3B)	11229(7)	3852(5)	6655(3)	583(20)
O(4A)	12017(5)	3254(4)	6586(2)	551(14)
O(4B)	11905(7)	3305(5)	6144(2)	597(22)

* $U_{eq}=1/3\Sigma_i \Sigma_j[U_{ij}(a_i^* a_j^*)a_i \cdot a_j]$. $\sigma U_{eq}=(1/6^{1/2})<\sigma U_{ii}/U_{ii}>U_{eq}$.

TABLE III-6

Complete distances (Å) for BTDD

C(1)-C(2)	1.397(4)
C(1)-C(6)	1.385(4)
C(1)-N(1)	1.433(3)
C(2)-C(3)	1.377(4)
C(2)-N(2)	1.427(3)
C(3)-C(4)	1.378(4)
C(4)-C(5)	1.373(4)
C(5)-C(6)	1.376(4)
C(7)-O(1A)	1.433(4)
C(7)-O(1B)	1.535(16)
C(7)-N(1)	1.421(4)
C(8)-N(1)	1.427(4)
C(8)-O(3A)	1.423(5)
C(8)-O(3B)	1.509(6)
C(9)-O(2A)	1.420(4)
C(9)-O(2B)	1.591(17)
C(9)-N(2)	1.426(3)
C(10)-N(2)	1.421(4)
C(10)-O(4A)	1.484(5)
C(10)-O(4B)	1.403(6)
O(1A)-O(2A)	1.481(4)
O(1B)-O(2B)	1.355(23)
O(3A)-O(4A)	1.466(5)
O(3B)-O(4B)	1.472(8)

TABLE III-7

Complete angles (°) for BTDD

C(6)-C(1)-C(2)	119.0(2)
N(1)-C(1)-C(2)	121.0(2)
N(1)-C(1)-C(6)	120.0(2)
C(3)-C(2)-C(1)	119.4(2)
N(2)-C(2)-C(1)	120.6(2)
N(2)-C(2)-C(3)	120.1(2)
C(4)-C(3)-C(2)	121.0(3)
C(5)-C(4)-C(3)	119.7(3)
C(6)-C(5)-C(4)	119.9(3)
C(5)-C(6)-C(1)	120.9(3)
N(1)-C(7)-O(1A)	116.7(2)
N(1)-C(7)-O(1B)	114.8(6)
O(3A)-C(8)-N(1)	117.8(3)
O(3B)-C(8)-N(1)	109.9(3)
N(2)-C(9)-O(2A)	115.7(2)
N(2)-C(9)-O(2B)	108.1(6)
O(4A)-C(10)-N(2)	113.2(3)
O(4B)-C(10)-N(2)	117.3(3)
O(2A)-O(1A)-C(7)	105.8(2)
O(2B)-O(1B)-C(7)	97.2(12)
O(1A)-O(2A)-C(9)	107.5(2)
O(1B)-O(2B)-C(9)	98.9(12)

TABLE III-7 Continued

C(7)-N(1)-C(1)	118.6(2)
C(8)-N(1)-C(1)	118.2(2)
C(8)-N(1)-C(7)	119.4(2)
C(9)-N(2)-C(2)	117.6(2)
C(10)-N(2)-C(2)	120.0(2)
C(10)-N(2)-C(9)	120.9(2)
O(4A)-O(3A)-C(8)	104.8(3)
O(4B)-O(3B)-C(8)	103.1(4)
O(3A)-O(4A)-C(10)	103.7(3)
O(3B)-O(4B)-C(10)	103.4(4)

TABLE III-8

Anisotropic thermal parameters for BTDD (in $Å^2$ X 10^4)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	397(15)	404(15)	357(14)	-41(13)	19(12)	24(12)
C(2)	386(14)	433(16)	329(14)	-14(12)	38(12)	32(13)
C(3)	600(19)	484(17)	367(15)	20(15)	32(14)	-53(14)
C(4)	725(21)	617(21)	390(15)	-119(17)	-71(16)	-65(15)
C(5)	593(20)	638(21)	517(19)	-74(17)	-176(15)	97(18)
C(6)	457(17)	479(18)	554(19)	26(14)	-56(14)	55(15)
C(7)	630(20)	615(20)	472(17)	79(16)	114(15)	-51(16)
C(8)	599(19)	464(17)	654(20)	-8(15)	6(16)	-93(16)
C(9)	546(19)	533(19)	481(17)	111(15)	-35(14)	29(15)
C(10)	367(17)	729(22)	661(20)	30(15)	40(14)	2(18)
N(1)	433(13)	424(13)	421(13)	-11(11)	49(10)	-53(11)
N(2)	352(12)	511(14)	408(13)	34(10)	-10(10)	36(11)

The form of the anisotropic parameter is

$$\exp[-2\pi^2(U_{11}h^2a^{*2}+....+2U_{23}klb^*c^*)].$$

TABLE III-9

Hydrogen parameters for BTDD (x,y,&z X10⁴)

atom	x	y	z	B
H(1)	5660	3228	5840	4.9
H(2)	5259	1966	5083	5.2
H(3)	7274	457	4891	5.3
H(4)	9707	198	5457	4.8
H(5A)	6724	2414	7064	5.6
H(5B)	6600	3094	7166	5.6
H(6A)	7583	3561	7317	5.6
H(6B)	8534	3259	7347	5.6
H(7A)	9714	4534	6855	5.6
H(7B)	9069	4914	6726	5.4
H(8A)	8829	4892	6302	5.6
H(8B)	9423	4524	6122	5.4
H(9A)	11336	717	7050	4.9
H(9B)	11417	248	6918	4.9
H(10A)	10265	-195	6699	4.9
H(10B)	9494	20	6739	4.9
H(11A)	12331	2246	5909	4.9
H(11B)	12860	1723	6015	5.4
H(12A)	13106	1643	6433	4.9
H(12B)	12729	2066	6634	5.4

Table III-10

Structure Factors for BTDD

The columns contain, in order, l, $10F_o$, $10F_c$, and $10\{(F_o^2-F_c^2)/\sigma(F_o^2)\}$.

0 0 1

2	784	821	-48
4	1479	1541	-42
6	462	498	-75
8	749	760	-15
10	229	259	-32
12	442	436	11
14	116	114	5
16	382	360	45
18	190	179	30
20	60	54	12
22	185	195	-25
24	26	33	-8
26	74	78	-6
28	30	16	11

0 2 1

0	1490	1777	-212
1	386	404	-46
2	181	195	-60
3	51	41	35
4	490	499	-17
5	1567	1613	-29
6	890	906	-17
7	17	3	8
8	695	684	14
9	64	64	1
10	53	62	-29
11	836	822	23
12	89	69	58
13	141	143	-6
14	-7	3	-2
15	70	74	-10
16	240	217	59
17	232	244	-34
18	-5	6	-2
19	36	51	-30
20	17	7	5
21	247	240	17
22	174	173	3
23	319	315	8
24	60	54	10
25	139	145	-15
26	144	127	38
27	217	218	-1
28	36	41	-6

0 4 1

0	678	717	-58
1	276	280	-11
2	2	22	-14
3	300	297	8
4	356	355	3
5	29	19	16
6	652	648	6
7	879	870	9
8	269	256	36
9	684	660	32
10	253	225	74
11	111	122	-37
12	152	155	-11
13	147	150	-8
14	125	116	28
15	135	150	-43
16	204	186	45
17	166	166	0
18	15	21	-4
19	136	145	-23
20	30	40	-14
21	226	218	19
22	29	49	-32
23	70	63	13
24	26	25	1
25	97	73	44
26	150	155	-12
27	24	32	-7

0 6 1

0	386	389	-5
1	9	5	2
2	-9	9	-6
3	142	141	2
4	281	272	24
5	159	136	67
6	240	230	27
7	30	5	26
8	222	226	-12
9	166	158	24
10	214	210	11
11	127	113	38
12	254	242	29
13	226	213	32
14	127	97	74
15	362	347	32
16	211	235	-65
17	18	1	7
18	64	81	-38
19	60	69	-18
20	83	108	-62
21	91	102	-25
22	31	48	-24
23	-13	7	-4
24	-9	15	-6
25	84	78	11

0 8 1

0	288	275	31
1	139	137	3
2	134	130	12
3	189	178	29
4	117	117	0
5	178	165	33
6	299	288	27
7	170	162	23
8	130	131	0
9	209	219	-25
10	213	195	44
11	56	66	-22
12	-30	17	-31
13	-36	7	-34
14	-12	28	-22
15	9	10	0
16	98	112	-36
17	11	25	-10
18	-13	3	-4
19	75	71	7
20	89	77	24
21	70	66	6
22	-32	5	-24

0 10 1

0	32	32	0
1	67	96	-75
2	31	44	-19
3	11	19	-5
4	278	274	7
5	324	315	18
6	96	83	28
7	140	136	7
8	26	16	9
9	273	262	23
10	95	84	22
11	150	147	6
12	134	129	12
13	29	7	15
14	57	44	21
15	65	47	29
16	-9	14	-6
17	2	1	0
18	-17	3	-6
19	74	73	3
20	30	26	6
21	30	31	-2
22	24	23	2
23	30	28	3
24	24	23	2
25	24	23	2
26	24	23	2
27	24	23	2
28	24	23	2

1 0 1

0	214	213	2
1	85	91	-13
2	81	84	-6
3	-10	10	-4
4	123	129	-14
5	135	125	22
6	-17	1	-6
7	48	57	-15
8	16	37	-22
9	27	20	5
10	-23	6	-12
11	12	32	-17

1 1 1

1	256	262	-26
2	1548	1618	-53
3	85	83	7
4	932	981	-62
5	281	296	-59
6	545	546	-1
7	892	905	-16
8	223	213	38
9	150	152	-6
10	489	483	15
11	28	18	22
12	338	323	46
13	139	133	26
14	53	33	56
15	107	102	21
16	285	262	70
17	122	115	25
18	-11	12	-10
19	47	50	-7
20	25	35	-18
21	139	135	14
22	159	150	32
23	147	135	37
24	83	81	7
25	163	161	7
26	51	43	16
27	64	65	-1
28	47	51	-9

1 2 1

1	742	777	-54
2	355	362	-21
3	642	647	-9
4	38	35	11
5	326	335	-29
6	427	455	-73
7	267	271	-15
8	582	591	-16
9	351	332	55
10	-12	28	-54
11	22	36	-8
12	105	115	-47
13	216	190	94
14	210	201	32
15	327	325	5
16	75	74	0
17	99	98	3
18	48	61	-41
19	74	75	-3
20	27	36	-16
21	135	135	0
22	-19	5	-14
23	47	57	-26
24	164	155	29
25	68	68	0
26	48	55	-15
27	80	73	21
28	10	12	0

1 3 1

1	19	17	3
2	1299	1334	-31
3	205	197	32
4	208	216	-31
5	561	551	20
6	178	181	-12
7	228	246	-74
8	254	257	-11
9	581	557	45
10	77	85	-41
11	178	168	41
12	93	94	-2
13	140	141	-5
14	231	224	26
15	99	95	16
16	149	132	62
17	20	17	4
18	58	43	39
19	120	113	25
20	30	29	1
21	192	185	21
22	96	76	57
23	39	41	-4
24	122	119	10
25	83	87	-11
26	37	27	15
27	76	76	0

1 4 1

1	338	338	-2
2	435	437	-6
3	157	164	-35
4	15	20	-9
5	147	150	-16
6	344	354	-30
7	43	46	-13
8	306	281	75
9	33	54	-79
10	84	78	25
11	191	190	5
12	-13	6	-9
13	48	85	38
14	142	131	44
15	356	330	66
16	153	139	53
17	111	90	74
18	92	85	24
19	94	94	1
20	-19	27	-38
21	125	126	-2
22	65	73	-21
23	75	65	25
24	128	126	7
25	-14	16	-14
26	13	8	3
27	89	83	16

	1	5	1		20	34	32	3	2	129	122	23	24	135	130	15
					21	-25	28	-47	3	106	103	7	25	110	106	10
1	135	125	43		22	63	65	-6	4	4	13	-4	26	21	45	-42
2	158	158	1		23	-19	19	-22	5	58	63	-13	27	-10	17	-11
3	122	134	-59		24	19	12	5	6	34	29	7				
4	181	176	22						7	124	122	7		2	2	1
5	352	338	38			1	8	1	8	51	47	8				
6	431	423	20						9	-17	2	-9	0	1362	1371	-8
7	156	151	23		1	56	45	30	10	36	32	6	1	712	720	-15
8	107	100	29		2	72	63	29	11	23	13	10	2	453	460	-15
9	106	107	-2		3	79	77	7	12	56	52	10	3	98	98	1
10	-19	0	-18		4	93	98	-21	13	27	27	0	4	914	911	4
11	48	65	-65		5	162	162	-1	14	-17	5	-9	5	282	286	-12
12	64	73	-33		6	144	146	-6	15	7	29	-22	6	263	272	-33
13	185	162	78		7	62	61	2					7	67	61	28
14	111	106	17		8	191	192	-3		1	12	1	8	124	125	-7
15	128	119	31		9	39	47	-22					9	114	130	-78
16	95	104	-35		10	-16	27	-36	1	86	85	3	10	58	64	-26
17	127	123	14		11	120	127	-28	2	151	143	26	11	211	207	14
18	61	64	-9		12	115	126	-38	3	15	6	5	12	196	189	26
19	108	108	0		13	35	41	-11	4	54	54	0	13	87	66	78
20	-31	13	-41		14	24	29	-7	5	29	37	-13	14	23	33	-24
21	54	35	39		15	45	49	-9	6	48	43	9	15	87	88	-5
22	10	28	-20		16	-13	39	-54	7	-18	23	-27	16	-5	8	-3
23	91	85	17		17	45	43	2	8	22	35	-19	17	148	149	-2
24	18	17	1		18	85	84	4	9	-21	0	-13	18	128	125	11
25	85	73	33		19	-22	14	-22	10	-11	8	-6	19	61	73	-39
26	26	37	-17		20	44	51	-14	11	-7	22	-15	20	4	27	-22
					21	-12	7	-6					21	8	5	1
	1	6	1		22	-13	1	-5		1	13	1	22	108	106	6
													23	28	28	0
1	229	219	35			1	9	1	1	70	72	-4	24	34	36	-5
2	306	301	17						2	12	6	3	25	14	14	0
3	283	282	3	1	-12	12	-11						26	21	38	-28
4	150	154	-20	2	72	77	-17		2	0	1		27	5	13	-3
5	34	32	7	3	-21	2	-18									
6	131	120	46	4	102	100	7	0	614	623	-15			2	3	1
7	54	42	36	5	29	23	10	2	302	293	28					
8	170	162	32	6	138	144	-18	4	49	51	-8	0	221	226	-21	
9	85	83	6	7	35	41	-12	6	143	148	-19	1	352	360	-24	
10	126	132	-24	8	16	24	-9	8	274	261	43	2	429	445	-41	
11	82	77	21	9	-34	1	-44	10	272	275	-12	3	97	103	-32	
12	-8	13	-9	10	74	70	11	12	142	141	5	4	275	250	82	
13	39	29	21	11	172	164	27	14	148	134	53	5	137	118	89	
14	79	73	21	12	141	131	32	16	257	262	-18	6	205	199	22	
15	135	118	58	13	143	130	41	18	103	131	-122	7	515	511	8	
16	21	30	-13	14	15	9	4	20	-17	17	-20	8	614	593	38	
17	91	80	34	15	-13	15	-12	22	407	386	47	9	432	393	92	
18	44	49	-12	16	-17	7	-11	24	53	46	16	10	63	71	-31	
19	68	71	-10	17	49	53	-10	26	24	37	-20	11	56	74	-74	
20	158	153	15	18	-26	5	-23	28	24	36	-18	12	127	119	33	
21	126	117	27	19	17	16	1					13	293	257	106	
22	-19	13	-17	20	54	75	-56		2	1	1	14	384	385	-2	
23	57	49	18									15	126	110	58	
24	17	0	8		1	10	1	0	43	48	-24	16	186	188	-7	
25	13	12	0					1	338	341	-9	17	146	131	55	
				1	122	128	-20	2	884	900	-20	18	24	28	-6	
	1	7	1	2	126	123	13	3	68	63	26	19	83	66	50	
				3	45	41	7	4	544	566	-46	20	115	106	27	
1	76	81	-19	4	80	70	28	5	608	624	-30	21	57	58	-3	
2	35	35	0	5	25	34	-15	6	471	473	-5	22	-28	10	-31	
3	47	50	-8	6	264	244	56	7	308	323	-51	23	76	78	-7	
4	-13	11	-14	7	108	100	25	8	88	71	75	24	25	21	4	
5	291	280	33	8	75	76	-4	9	323	316	19	25	-20	7	-15	
6	57	53	13	9	73	77	-9	10	23	48	-90	26	42	45	-7	
7	354	341	35	10	61	70	-25	11	133	151	-89	27	30	12	18	
8	41	37	9	11	42	45	-5	12	129	113	69					
9	84	87	-11	12	-16	19	-20	13	103	112	-39		2	4	1	
10	230	221	28	13	81	86	-15	14	10	11	-1					
11	73	52	62	14	17	24	-8	15	101	110	-36	0	406	414	-20	
12	10	0	4	15	64	64	0	16	245	241	15	1	500	492	17	
13	-7	19	-15	16	59	64	-14	17	251	242	28	2	59	77	-97	
14	99	118	-71	17	18	19	0	18	281	276	17	3	65	53	51	
15	37	38	-1	18	-19	3	-10	19	155	148	25	4	558	557	2	
16	-15	17	-17					20	346	347	-2	5	168	152	67	
17	186	180	17		1	11	1	21	108	104	14	6	298	279	58	
18	-25	1	-21					22	32	6	28	7	14	19	-9	
19	-15	19	-19	1	108	109	-3	23	7	1	1	8	169	156	51	

9	308	303	15	0	40	49	-27	3	9	33	-32	14	-14	18	-22
10	184	175	32	1	133	141	-33	4	-6	20	-14	15	151	145	23
11	90	81	39	2	33	39	-16	5	66	79	-43	16	234	226	27
12	265	259	18	3	87	85	5	6	96	98	-8	17	58	50	23
13	38	48	-30	4	268	257	33	7	41	44	-7	18	180	186	-20
14	87	71	57	5	232	226	18	8	-22	13	-22	19	94	92	6
15	303	306	-7	6	17	2	10	9	31	35	-7	20	276	281	-14
16	80	92	-45	7	88	93	-18	10	12	21	-8	21	52	37	32
17	147	158	-42	8	30	22	14	11	22	33	-17	22	53	60	-18
18	15	18	-3	9	99	104	-17	12	23	13	9	23	25	30	-7
19	46	52	-15	10	64	60	11	13	74	72	3	24	30	40	-18
20	26	28	-3	11	95	92	8	14	31	25	9	25	5	21	-13
21	194	194	1	12	211	210	2	15	63	53	25	26	84	72	31
22	37	40	-6	13	190	183	24	16	-17	1	-8	27	22	24	-2
23	82	76	17	14	61	78	-52	17	61	54	16				
24	34	39	-9	15	13	27	-17						3 2 1		
25	49	44	9	16	33	32	0		2 11 1						
26	27	24	2	17	77	74	8					1	172	165	33
				18	49	44	9	0	119	114	17	2	129	132	-11
	2 5 1			19	36	64	-72	1	51	40	22	3	36	49	-51
				20	-25	18	-32	2	64	64	0	4	179	161	73
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				14	45	58	-34	18	36	27	13	11	19	28	-11				
	5	8	1	15	15	7	5	19	39	46	-14	12	-3	5	-1				
				16	134	142	-24												
1	-15	12	-12	17	-17	14	-16		6	5	1		6	9	1				
2	12	26	-16	18	33	31	2												
3	127	140	-45	19	-14	14	-12	0	60	69	-27	0	79	85	-17				
4	47	54	-17	20	12	26	-14	1	119	109	33	1	72	65	18				
5	34	33	1	21	-26	12	-25	2	49	62	-36	2	17	18	-1				
6	69	101	-113					3	87	81	21	3	24	10	12				
7	43	32	21		6	2	1	4	186	200	-46	4	-20	1	-12				
8	65	48	39					5	24	9	15	5	-10	26	-23				
9	9	6	1	0	84	57	80	6	71	64	19	6	81	82	-4				
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12	101	100	3	3	144	132	39	9	49	48	0								
13	-29	3	-28	4	121	119	8	10	25	42	-32		7	0	1				
14	-11	37	-44	5	12	5	4	11	-17	19	-21								
15	-17	23	-25	6	87	83	13	12	20	15	4	2	62	56	14				
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				8	30	48	-42	14	35	33	3	6	242	238	12				
	5	9	1	9	76	84	-23	15	-15	13	-12	8	66	80	-43				
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3	90	95	-16	13	45	45	0					16	25	19	6				
4	32	17	19	14	68	79	-32		6	6	1	18	9	22	-11				
5	145	152	-21	15	60	68	-22												
6	31	44	-24	16	5	23	-15	0	111	111	0		7	1	1				
7	123	126	-12	17	32	43	-20	1	14	6	4								
8	80	87	-21	18	30	22	11	2	46	49	-9	1	85	19	25				
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11	-7	33	-33	21	3	33	-28	5	84	75	26	4	31	39	-15				
12	22	20	1					6	167	164	7	5	78	79	-3				
13	18	4	8		6	3	1	7	42	45	-7	6	161	159	6				
								8	37	42	-11	7	20	38	-32				
	5	10	1	0	233	226	22	9	-23	25	-38	8	75	78	-8				
				1	101	93	26	10	106	111	-15	9	42	40	5				
1	-33	22	-53	2	33	34	0	11	72	92	-67	10	145	150	-15				
2	-9	33	-34	3	-12	5	-6	12	-10	32	-34	11	22	6	12				
3	40	38	2	4	95	89	22	13	-18	16	-18	12	-12	5	-6				
4	-16	11	-12	5	76	87	-39	14	27	34	-11	13	17	26	-10				
5	-22	19	-27	6	103	98	17	15	29	26	3	14	-8	1	-2				
6	16	16	0	7	110	106	15	16	35	32	3	15	-15	7	-9				
7	56	61	-10	8	170	170	0	17	25	20	5	16	24	25	0				
8	45	48	-5	9	34	46	-27					17	23	19	3				
9	36	34	4	10	157	150	25		6	7	1	18	-25	11	-21				
				11	-6	0	-1												
	6	0	1	12	102	115	-51	0	59	59	0		7	2	1				
				13	122	128	-18	1	170	183	-44								

1	256	249	20	13	66	78	-35	2	31	38	-12	2	-28	4	-27
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3	129	137	-28	15	71	82	-30	4	18	25	-8	4	-14	9	-9
4	16	16	0	16	24	33	-13	5	38	48	-20	5	-2	2	0
5	59	57	6									6	95	94	3
6	25	28	-5		7 5 1				8 0 1			7	54	42	24
7	35	35	-1									8	40	52	-27
8	-14	27	-29	1	24	44	-37	0	107	92	43	9	7	7	0
9	27	26	1	2	-24	4	-20	2	80	68	33	10	35	29	10
10	73	83	-33	3	26	25	1	4	294	288	15	11	35	35	0
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13	15	14	0	6	-20	16	-22	10	66	59	18				
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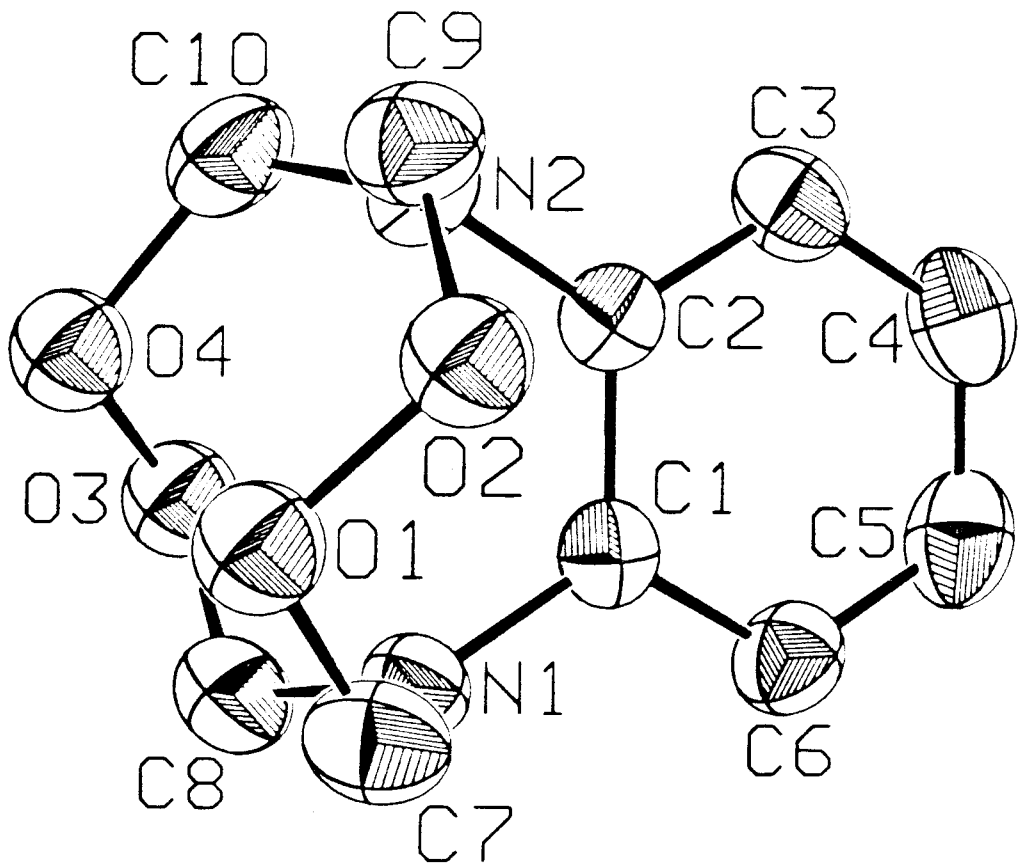
15	15	32	-23	8	30	45	-29					1	-12	17	-14
16	-23	15	-24	9	46	52	-13		8 1 1			2	-31	17	-42
17	-13	24	-22	10	15	37	-31					3	20	1	11
				11	44	62	-44	0	124	123	2	4	84	82	4
	7 3 1			12	-11	11	-7	1	98	105	-21	5	35	38	-6
				13	25	27	-3	2	21	20	1	6	-15	21	-20
1	108	115	-23	14	21	12	8	3	28	25	3	7	34	40	-11
2	123	115	27					4	81	75	16	8	14	23	-8
3	32	43	-24		7 6 1			5	31	28	5	9	28	28	0
4	34	38	-8					6	169	166	9	10	38	49	-21
5	88	83	14	1	-8	18	-11	7	20	11	7				
6	77	85	-24	2	34	28	8	8	68	54	33		8 5 1		
7	68	71	-8	3	-11	19	-15	9	25	24	1				
8	120	124	-15	4	63	83	-61	10	116	112	13	0	97	101	-13
9	55	70	-43	5	47	45	3	11	19	6	9	1	63	49	31
10	27	37	-17	6	143	162	-63	12	43	44	-2	2	24	35	-18
11	34	48	-29	7	39	49	-22	13	36	30	9	3	62	62	0
12	35	30	8	8	38	45	-14					4	-18	7	-12
13	36	40	-8	9	44	39	10		8 2 1			5	13	30	-20
14	-20	0	-13	10	24	23	1					6	-17	5	-9
15	-16	10	-11	11	-28	8	-27	0	100	99	1	7	-18	1	-9
16	21	22	0	12	53	56	-6	1	43	35	15				
17	9	3	1					2	19	22	-3		8 6 1		
					7 7 1			3	9	24	-15				
	7 4 1							4	70	73	-8	0	116	121	-16
				1	79	68	29	5	63	67	-12	1	43	56	-27
1	50	55	-12	2	14	15	-1	6	25	2	17	2	15	22	-6
2	54	54	1	3	76	64	30	7	112	114	-7	3	56	40	29
3	56	52	10	4	54	42	27	8	51	47	10				
4	85	93	-25	5	17	18	-1	9	39	28	19		9 0 1		
5	61	65	-11	6	44	44	-1	10	-14	17	-14				
6	-21	12	-19	7	29	29	0	11	13	19	-6	2	-12	19	-14
7	19	29	-14	8	54	60	-15	12	21	27	-7				
8	33	41	-16	9	-23	12	-20						9 1 1		
9	-17	9	-12						8 3 1						
10	35	30	8		7 8 1							1	-12	0	-4
11	12	19	-6					0	29	52	-52	2	47	45	3
12	28	45	-33	1	59	44	31	1	35	33	3				



An ORTEP drawing of BTDD.

Figure III-7

Table III-11

Atomic parameters for CTDD (X 10^4; U_{eq} in $Å^2$ X 10^4)

atom	x	y	z	U_{eq}
C(1)	7891(4)	4108(4)	2113(3)	348(7)
C(2)	5572(4)	4649(3)	2693(3)	328(6)
C(3)	4296(5)	6095(4)	1739(3)	452(8)
C(4)	5067(6)	7725(4)	1344(3)	510(9)
C(5)	7379(6)	7239(4)	864(3)	514(9)
C(6)	8633(5)	5745(4)	1797(3)	440(7)
C(7)	9730(5)	840(4)	2536(4)	550(10)
C(8)	9416(5)	2565(5)	4085(4)	541(9)
C(9)	4766(5)	2001(5)	2529(4)	523(9)
C(10)	4599(5)	2555(4)	4611(3)	458(8)
N(1)	9214(4)	2517(3)	2870(3)	418(7)
N(2)	4765(4)	3136(3)	3267(2)	362(5)
O(1)	8094(4)	29(3)	2807(3)	642(7)
O(2)	6733(4)	1125(3)	1868(3)	702(7)
O(3)	7568(4)	2893(3)	4988(2)	608(6)
O(4)	6579(4)	1551(3)	5099(2)	537(6)

$U_{eq}=1/3\,\Sigma_i\Sigma_j[U_{ij}(a_i^*a_j^*)\,a_i\cdot a_j]$. $\sigma U_{eq}=(1/6^{1/2})\langle\sigma U_{ii}/U_{ii}\rangle U_{eq}$

Table III-12

Complete distances (Å) for CTDI

C(1)-C(2)	1.537(4)
C(1)-C(6)	1.523(4)
C(1)-N(1)	1.463(4)
C(2)-C(3)	1.518(4)
C(2)-N(2)	1.460(4)
C(3)-C(4)	1.523(5)
C(4)-C(5)	1.509(5)
C(5)-C(6)	1.511(5)
C(7)-N(1)	1.416(5)
C(7)-O(1)	1.444(5)
C(8)-N(1)	1.405(5)
C(8)-O(3)	1.421(5)
C(9)-N(2)	1.398(4)
C(9)-O(2)	1.425(5)
C(10)-N(2)	1.427(4)
C(10)-O(4)	1.468(4)
O(1)-O(2)	1.458(4)
O(3)-O(4)	1.452(4)

Table III-13

Complete angles (°) for CTDD

C(6)-C(1)-C(2)	108.7(2)
N(1)-C(1)-C(2)	114.3(2)
N(1)-C(1)-C(6)	113.5(3)
C(3)-C(2)-C(1)	109.9(2)
N(2)-C(2)-C(1)	114.3(2)
N(2)-C(2)-C(3)	114.0(2)
C(4)-C(3)-C(2)	109.8(3)
C(5)-C(4)-C(3)	112.4(3)
C(6)-C(5)-C(4)	112.0(3)
C(5)-C(6)-C(1)	110.1(3)
O(1)-C(7)-N(1)	117.3(3)
O(3)-C(8)-N(1)	117.3(3)
O(2)-C(9)-N(2)	116.7(3)
O(4)-C(10)-N(2)	115.5(3)
C(7)-N(1)-C(1)	118.1(3)
C(8)-N(1)-C(1)	119.4(3)
C(8)-N(1)-C(7)	119.7(3)
C(9)-N(2)-C(2)	120.3(3)
C(10)-N(2)-C(2)	116.8(2)
C(10)-N(2)-C(9)	120.2(3)
O(2)-O(1)-C(7)	104.0(2)
O(1)-O(2)-C(9)	107.7(3)
O(4)-O(3)-C(8)	108.5(2)
O(3)-O(4)-C(10)	105.3(2)

Table III-14

Anisotropic thermal parameters for CTDD (in $Å^2$ X 10^4)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	387(17)	295(15)	356(16)	-117(13)	-70(13)	-37(12)
C(2)	356(16)	287(15)	360(16)	-122(13)	-103(13)	-29(12)
C(3)	439(18)	419(18)	476(19)	-91(15)	-173(15)	-33(15)
C(4)	645(23)	305(17)	504(21)	-100(15)	-175(17)	43(15)
C(5)	713(24)	352(17)	475(20)	-245(17)	-85(17)	15(15)
C(6)	432(18)	422(18)	487(19)	-201(15)	-29(15)	-75(15)
C(7)	453(20)	377(18)	678(24)	-53(15)	-41(18)	-32(17)
C(8)	420(20)	518(21)	627(24)	-134(16)	-215(18)	63(17)
C(9)	494(21)	473(20)	676(24)	-212(16)	-113(18)	-138(18)
C(10)	438(19)	412(17)	511(21)	-189(15)	-65(16)	-10(15)
N(1)	351(14)	340(14)	510(17)	-63(11)	-82(12)	-55(12)
N(2)	386(14)	342(13)	401(15)	-183(11)	-82(11)	-38(11)
O(1)	741(17)	401(13)	777(19)	-190(12)	-152(14)	-72(12)
O(2)	876(20)	641(17)	725(19)	-322(15)	-154(16)	-217(14)
O(3)	650(17)	669(16)	589(16)	-272(13)	-245(13)	-53(13)
O(4)	611(15)	464(13)	537(15)	-228(11)	-218(12)	81(11)

The form of the anisotropic thermal parameter is

$$\exp[-2\pi^2(U_{11}h^2a^{*2}+....+2U_{23}klb^*c^*)].$$

Table III-15

Hydrogen parameters for CTDD (x,y,&z X10⁴; B in Å²)

atom	x	y	z	B
H(1)	2872	6442	2105	3.0
H(2)	4447	5629	1014	3.0
H(3)	4781	8251	2053	3.0
H(4)	4351	8565	687	3.0
H(5)	7784	8281	734	3.0
H(6)	7634	6878	91	3.0
H(7)	8480	6138	2550	3.0
H(8)	10067	5421	1428	3.0
H(9)	8018	3729	1354	3.0
H(10)	5429	5159	3397	3.0
H(11)	10843	14	2972	3.0
H(12)	10214	1002	1646	3.0
H(13)	9985	3505	3996	3.0
H(14)	10347	1451	4426	3.0
H(15)	3877	2698	1917	3.0
H(16)	4222	1091	3070	3.0
H(17)	3734	1802	4880	3.0
H(18)	3956	3589	4972	3.0

Table III-16

Structure Factors for CTDD

The columns contain, in order, l, $10F_o$, $10F_c$, and $10\{(F_o^2-F_c^2)/\sigma(F_o^2)\}$.

-7 1 1

1	-9	4	-15
2	-7	0	-7

-6 1 1

1	5	4	2
2	12	15	-11
3	-5	11	-21
4	-7	4	-10
5	16	12	13

-6 2 1

1	-3	8	-10
2	25	22	12
3	18	20	-7
4	-10	6	-21

-6 3 1

1	62	64	-15
2	15	15	-1
3	52	48	24

-5 1 1

1	17	17	-1
2	32	33	-3
3	-1	7	-10
4	32	41	-61
5	22	21	5
6	24	19	19
7	-11	6	-27
8	-4	9	-13

-5 2 1

1	12	7	12
2	-6	22	-87
3	24	22	11
4	-5	9	-18
5	25	22	15
6	43	34	48
7	6	9	-6

-5 3 1

1	40	47	-50
2	29	31	-7
3	14	28	-76
4	8	7	2
5	23	29	-32
6	-5	11	-22

-5 4 1

1	8	5	5
2	21	16	19
3	21	16	18
4	23	24	-3
5	2	4	-1

-5 5 1

1	28	25	16

-4 1 1

1	40	49	-74
2	5	11	-17
3	57	57	-5
4	13	13	0
5	-6	3	-8
6	50	43	47
7	-6	6	-13
8	17	18	-2
9	18	21	-13

-4 2 1

1	128	143	-99
2	37	38	-2
3	58	56	19
4	13	11	6
5	3	8	-11
6	46	40	39
7	57	49	46
8	7	10	-7
9	17	19	-6

-4 3 1

1	116	121	-34
2	32	36	-27
3	-2	0	0
4	17	26	-50
5	14	11	10
6	22	20	7
7	-8	0	-10
8	13	23	-46

-4 4 1

1	15	9	19
2	127	126	3
3	75	82	-44
4	25	34	-52
5	29	28	8
6	37	38	-5
7	5	5	0

-4 5 1

1	63	57	40
2	14	16	-8
3	10	6	8
4	23	30	-41
5	-5	7	-11
6	11	19	-28

-4 6 1

1	36	31	25
2	35	33	9
3	-10	3	-18

-3 1 1

1	72	91	-197
2	118	126	-62
3	204	233	-157
4	171	175	-24
5	105	104	5
6	55	54	8
7	70	66	28
8	20	19	5
9	38	38	1
10	18	17	3

-3 2 1

1	20	16	25
2	40	56	-170
3	11	13	-7
4	53	59	-55
5	16	20	-23
6	5	9	-10
7	28	26	10
8	49	58	-70
9	7	2	7
10	40	38	11

-3 3 1

1	94	97	-25
2	43	51	-72
3	44	55	-92
4	5	12	-23
5	35	33	14
6	93	94	-8
7	3	7	-6
8	9	2	12
9	10	0	13
10	28	29	-3

-3 4 1

1	78	71	45
2	48	45	16
3	85	100	-119
4	-4	6	-11
5	33	42	-62
6	8	10	-6
7	17	25	-42
8	37	45	-54
9	-2	5	-4

-3 5 1

1	0	4	-3
2	97	99	-12
3	50	51	-5
4	37	50	-97
5	33	42	-63
6	48	59	-72
7	40	40	-2
8	-11	5	-24

-3 6 1

1	35	31	23
2	8	1	9
3	61	65	-21
4	8	9	-2
5	8	16	-28
6	15	12	8

-3 7 1

1	49	47	12
2	28	18	41
3	22	13	34

-2 1 1

1	-5	11	-29
2	304	437	--
3	156	171	-102
4	227	228	-6
5	112	115	-22
6	176	161	78
7	-6	5	-14
8	20	20	4
9	24	21	13
10	25	19	30
11	3	7	-6

-2 2 1

1	-6	1	-10
2	60	103	--
3	23	36	-135
4	116	121	-32
5	67	66	3
6	24	17	40
7	94	84	72
8	43	43	-6
9	29	21	43
10	38	26	60
11	10	4	13

-2 3 1

1	37	46	-86
2	19	18	1
3	33	39	-58
4	74	99	-236
5	60	72	-109
6	116	121	-34
7	44	43	7
8	146	131	81
9	46	53	-54
10	14	11	8
11	31	31	3

-2 4 1

1	96	94	10
2	20	21	-5
3	14	22	-45
4	33	39	-43
5	60	63	-29
6	1	1	0
7	6	5	2
8	9	15	-23
9	69	59	60
10	24	24	-1

-2 5 1

1	39	33	37
2	27	24	19
3	14	3	31
4	-11	8	-37
5	24	29	-34
6	16	16	2
7	17	13	13
8	12	9	10
9	-4	2	-3
10	47	39	46

-2 6 1

1	110	103	44
2	19	19	1
3	31	23	42
4	40	48	-57
5	20	19	3
6	-6	0	-6
7	36	26	51
8	14	14	2

-2 7 1

1	83	82	6
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3	92	90	20									0	72	71	8				
4	57	52	42	-5	23	27	-21	0	22	26	-33	1	67	65	15				
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8	38	42	-28	-1	51	51	0	4	36	42	-48	5	53	52	9				
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8	63	64	-6					6	21	20	4	5	17	14	14				
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11	-15	3	-47	0	38	38	-6					8	46	46	4				
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	6 4 1			2	-4	2	-5												
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7	37	33	30	3	40	38	9						7 7 1						
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9	30	31	-7	5	20	25	-27					1	19	16	12				
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	6 5 1							0	56	54	19	5	-2	17	-52				
					7 -1 1			1	25	25	2	6	8	14	-20				
-4	7	16	-25					2	65	65	0	7	19	21	-9				
-3	-13	2	-28	0	12	9	10	3	78	68	70								
-2	17	19	-7	1	47	46	8	4	19	20	-7		8 2 1						
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5	4	2	1						7 4 1										
6	35	37	-10	-3	12	3	15						8 3 1						
7	20	25	-32	-2	-9	6	-19	-3	11	14	-9								
8	83	83	1	-1	20	22	-8	-2	33	37	-18	0	17	15	10				
9	32	33	-5	0	36	27	63	-1	42	40	14	1	9	3	12				
10	-3	2	-2	1	41	33	49	0	46	44	21	2	10	4	12				
				2	-5	1	-6	1	6	11	-15	3	-5	4	-7				
	6 6 1			3	32	32	1	2	39	35	31	4	22	26	-19				
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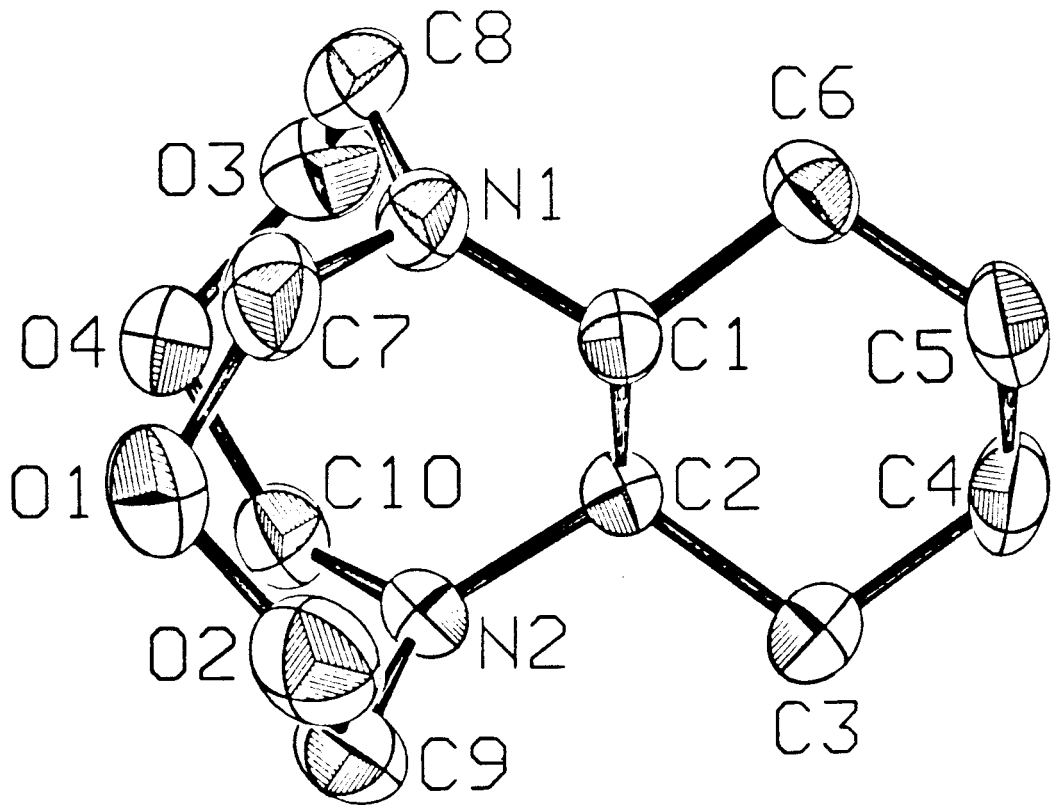
-3	-14	1	-34	5	25	22	17	4	68	65	26								
-2	42	45	-13	6	17	15	9	5	12	14	-5		8 4 1						
-1	14	14	1	7	22	25	-16	6	87	84	17								
0	41	43	-12					7	46	43	19	1	-6	5	-10				
1	23	25	-17		7 1 1			8	41	40	5	2	10	5	12				
2	-8	2	-14					9	38	38	-2	3	-6	1	-7				
3	42	42	-1	-4	15	12	9					4	39	33	39				
4	98	101	-22	-3	19	22	-16		7 5 1			5	16	13	12				
5	107	104	17	-2	-12	14	-54					6	73	69	25				
6	36	32	24	-1	28	35	-39	-2	-11	3	-19								
7	49	47	12	0	44	44	-1	-1	10	8	4		8 5 1						
8	2	13	-27	1	97	85	76	0	-8	9	-37								
9	51	54	-18	2	-10	4	-26	1	17	21	-20	2	30	24	31				
10	19	24	-26	3	-6	10	-26	2	40	40	5	3	25	25	-2				
				4	34	25	53	3	59	60	-7	4	9	7	3				
	6 7 1			5	37	34	15	4	26	29	-14	5	36	33	16				



An ORTEP drawing of CTDD.

Figure III-8

Table III-17

Atomic parameters for HMDD (X 10^4; U and U_{eq} in $Å^2$ X 10^4)

atom	x	y	z	U_{eq} or U
C(1)	10659(1)	5503(2)	2533(1)	327(3)*
C(2)	10747(1)	2522(2)	1115(1)	323(2)*
C(3)	8315(1)	1851(2)	1728(1)	334(3)*
N(1)	11134(1)	3345(2)	2305(1)	275(2)*
O(1)	9482(1)	2326(1)	546(1)	355(2)*
O(2)	9071(1)	624(1)	1219(1)	364(2)*
H(1)	11138(13)	6028(22)	3298(14)	318(27)
H(2)	10772(12)	6636(23)	1940(12)	311(27)
H(3)	11108(12)	1065(22)	1096(12)	296(26)
H(4)	10947(12)	3569(22)	585(12)	316(28)
H(5)	7745(13)	2729(24)	1069(12)	278(25)
H(6)	7928(11)	605(22)	2002(10)	255(25)

* $U_{eq}=1/3\Sigma_i \Sigma_j[U_{ij}(a_i^* a_j^*) a_i \cdot a_j]$. $\sigma U_{eq}=(1/6^{1/2})<\sigma U_{ii}/U_{ii}>U_{eq}$

Table III-18

Complete Distances (Å) for HMDD

C(1)-N(1)	1.449(2)
C(1)-H(1)	0.945(15)
C(1)-H(2)	1.010(14)
C(1)-C(1)	1.550(2)*
C(2)-N(1)	1.415(1)
C(2)-O(1)	1.433(1)
C(2)-H(3)	0.960(14)
C(2)-H(4)	0.966(14)
C(3)-O(2)	1.440(1)
C(3)-H(5)	0.988(14)
C(3)-H(6)	0.978(13)
C(3)-N(1)	1.417(2)
O(1)-O(2)	1.465(1)

* These atoms are related by symmetry (a 2-fold axis).

Table III-19

Complete Angles (°) for HMDD

H(1)-C(1)-N(1)	108.6(9)
H(2)-C(1)-N(1)	106.9(8)
C(1)-C(1)-N(1)	116.5(1)*
H(2)-C(1)-H(1)	106.0(12)
C(1)-C(1)-H(1)	108.5(9)
C(1)-C(1)-H(2)	109.9(8)
O(1)-C(2)-N(1)	115.5(1)
H(3)-C(2)-N(1)	109.4(8)
H(4)-C(2)-N(1)	111.5(8)
H(3)-C(2)-O(1)	109.0(8)
H(4)-C(2)-O(1)	101.4(8)
H(4)-C(2)-H(3)	109.8(12)
H(5)-C(3)-O(2)	106.7(8)
H(6)-C(3)-O(2)	101.7(8)
N(1)-C(3)-O(2)	117.8(1)
H(6)-C(3)-H(5)	112.3(11)
N(1)-C(3)-H(5)	108.9(8)
N(1)-C(3)-H(6)	109.4(8)
C(2)-N(1)-C(1)	118.1(1)
C(3)-N(1)-C(1)	119.4(1)
C(3)-N(1)-C(2)	120.2(1)
O(2)-O(1)-C(2)	107.0(1)
O(1)-O(2)-C(3)	105.3(1)

Table III-20

Anisotropic thermal parameters for HMDD (in $Å^2$ X 10^4)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	366(7)	241(6)	397(7)	-51(4)	162(5)	-24(5)
C(2)	321(6)	374(7)	309(6)	-7(5)	154(5)	-15(5)
C(3)	246(6)	404(7)	345(6)	-41(5)	92(5)	-31(5)
N(1)	269(5)	277(5)	290(5)	-9(3)	110(5)	-13(3)
O(1)	348(5)	451(5)	259(5)	-35(3)	96(4)	13(3)
O(2)	407(5)	329(5)	387(15	-81(3)	176(4)	-69(3)

The form of the anisotropic thermal parameter is

$$\exp[-2\pi^2(U_{11}h^2a^{*2}+....+2U_{23}klb^*c^*)].$$

Table III-21

Structure Factors for HMDD

The columns contain, in order, l, $10F_o$, $10F_c$, and $10\{(F_o^2-F_c^2)/\sigma(F_o^2)\}$.

	h 0 0		
2	865	816	65
4	751	781	-47
6	692	670	37
8	315	320	-17
10	-6	8	-35
12	90	79	88
	h 0 2		
-12	86	82	30
-10	53	52	10
-8	179	176	18
-6	123	121	14
-4	518	519	-1
-2	348	339	28
0	538	584	-103
2	590	619	-57
4	407	403	10
6	104	108	-41
8	28	31	-34
10	134	133	1
12	8	4	9
	h 0 4		
-14	98	90	60
-12	167	172	-25
-10	254	255	-5
-8	97	102	-45
-6	5	0	14
-4	429	427	7
-2	17	12	62
0	171	190	-133
2	121	110	91
4	451	455	-12
6	158	155	17
8	37	42	-56
10	45	46	-8
	h 0 6		
-14	-7	7	-26
-12	287	289	-6
-10	119	124	-40
-8	223	221	9
-6	15	15	4
-4	16	0	90
-2	338	343	-19
0	463	440	56
2	401	390	35
4	151	145	37
6	513	509	9
8	156	154	11
10	85	76	67
	h 0 8		
-12	83	76	53
-10	249	248	5
-8	50	50	-6
-6	359	348	35
-4	386	383	9
-2	198	198	2
0	180	172	49
2	319	322	-8
4	95	93	20
6	212	213	-2
8	50	48	19
	h 0 10		
-12	79	79	-4
-10	120	123	-21
-8	198	198	0
-6	15	9	35

-4	75	76	-5
-2	11	7	20
0	153	153	4
2	211	217	-27
4	21	19	16
	h 0 12		
-10	165	165	-1
-8	48	45	30
-6	344	336	26
-4	170	169	5
-2	99	100	-10
0	45	49	-44
2	59	58	12
	h 0 14		
-6	36	35	8
-4	170	158	61
	h 1 0		
1	16	17	-34
3	170	181	-83
5	35	32	51
7	3	3	1
9	17	17	0
11	87	91	-37
13	20	22	-25
	h 1 1		
-13	29	29	-7
-11	35	37	-29
-9	70	69	22
-7	187	187	0
-5	68	70	-19
-3	291	297	-29
-1	942	871	92
1	511	553	-110
3	495	480	38
5	400	386	45
7	238	235	13
9	57	56	12
11	81	76	53
	h 1 2		
-13	83	87	-42
-11	10	20	-105
-9	131	131	1
-7	12	9	35
-5	353	355	-5
-3	346	340	23
-1	108	108	-3
1	737	765	-48
3	437	443	-17
5	198	204	-40
7	181	185	-25
9	83	87	-48
11	23	26	-35
	h 1 3		
-13	8	13	-35
-11	-4	1	-9
-9	242	242	3
-7	498	485	34
-5	214	216	-10
-3	682	712	-58
-1	525	520	11
1	624	657	-70
3	51	55	-66
5	308	313	-16
7	233	232	2
9	195	202	-48
11	50	54	-51

	h 1 4		
-13	-5	5	-20
-11	96	92	39
-9	41	41	-1
-7	233	234	-3
-5	381	376	19
-3	45	44	15
-1	553	545	17
1	705	680	44
3	113	115	-18
5	388	386	6
7	116	119	-24
9	27	21	63
11	54	50	43
	h 1 5		
-13	129	125	38
-11	324	321	11
-9	32	35	-33
-7	153	147	42
-5	117	117	-1
-3	191	197	-41
-1	292	288	15
1	205	194	62
3	165	170	-31
5	90	94	-47
7	128	128	1
9	84	87	-38
	h 1 6		
-13	76	70	55
-11	23	26	-42
-9	197	198	-5
-7	183	177	44
-5	19	16	42
-3	116	119	-26
-1	232	230	8
1	159	146	94
3	149	156	-60
5	87	85	18
7	15	12	21
9	16	14	13
	h 1 7		
-13	69	66	30
-11	18	11	57
-9	280	281	-4
-7	144	140	29
-5	62	63	-10
-3	29	29	13
-1	26	27	-3
1	92	83	99
3	39	40	-15
5	320	324	-15
7	133	131	16
9	127	122	40
	h 1 8		
-13	-9	7	-52
-11	158	162	-24
-9	129	130	-11
-7	115	112	33
-5	152	148	33
-3	41	39	28
-1	16	19	-47
1	39	36	42
3	46	46	0
5	39	40	-7
7	54	55	-19
	h 1 9		

-13	3	4	-1
-11	102	104	-24
-9	112	112	0
-7	120	117	27
-5	212	213	-7
-3	306	307	-4
-1	169	168	9
1	207	214	-43
3	202	207	-25
5	12	11	6
7	66	61	45
	h 1 10		
-11	63	66	-36
-9	50	52	-17
-7	93	95	-22
-5	94	92	17
-3	148	150	-18
-1	31	28	38
1	122	121	8
3	89	88	15
5	34	32	30
	h 1 11		
-11	119	116	23
-9	43	48	-81
-7	178	177	2
-5	282	282	0
-3	20	22	-22
-1	67	73	-83
1	39	39	-1
3	46	42	55
	h 1 12		
-9	16	17	-12
-7	76	74	26
-5	104	101	29
-3	6	8	-9
-1	99	99	0
1	93	92	16
	h 1 13		
-9	26	25	11
-7	128	126	15
-5	75	76	-14
-3	130	130	-5
-1	85	91	-72
	h 2 0		
0	545	538	14
2	127	130	-24
4	17	19	-43
6	68	72	-56
8	110	111	-9
10	124	122	12
12	28	27	16
	h 2 1		
-12	131	132	-11
-10	106	105	6
-8	249	257	-36
-6	41	42	-22
-4	161	154	55
-2	459	455	11
0	375	381	-22
2	274	279	-23
4	104	112	-94
6	-2	3	-11
8	150	156	-47
10	27	27	5
12	76	72	42

h 2 2				-8	47	48	-17	5	276	276	1				
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-12	9	0	30	-4	53	53	3	9	247	252	-24	-9	80	80	1
-10	198	202	-24	-2	161	159	11	11	18	16	21	-7	198	202	-24
-8	541	535	13	0	44	40	48					-5	38	33	74
-6	384	385	-3	2	38	38	-6	h 3 1				-3	441	432	26
-4	540	519	48	4	-5	3	-20					-1	115	114	11
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0	324	327	-11	8	16	16	-1	-9	54	52	37	3	10	14	-34
2	132	134	-19					-7	89	85	39	5	8	9	-6
4	72	76	-60	h 2 8				-5	105	107	-25	7	41	39	23
6	26	29	-37					-3	18	13	69				
8	37	38	-6	-12	-8	3	-29	-1	177	167	66	h 3 7			
10	60	61	-12	-10	161	162	-8	1	228	222	35				
				-8	178	180	-16	3	183	181	9	-11	46	44	26
h 2 3				-6	37	40	-51	5	27	27	-3	-9	95	97	-16
				-4	112	113	-18	7	282	278	16	-7	79	81	-14
-12	96	96	-1	-2	385	384	4	9	273	269	18	-5	168	165	24
-10	170	175	-32	0	265	261	16	11	33	36	-43	-3	275	265	45
-8	219	211	42	2	44	50	-95					-1	31	29	23
-6	15	5	101	4	78	78	2	h 3 2				1	115	112	25
-4	247	244	16	6	51	47	47					3	124	120	30
-2	298	285	52					-11	6	9	-19	5	96	100	-42
0	316	308	33	h 2 9				-9	117	121	-43	7	39	43	-53
2	383	383	0					-7	59	61	-35				
4	283	278	25	-12	92	90	22	-5	75	71	46	h 3 8			
6	177	174	21	-10	48	48	6	-3	46	39	107				
8	96	95	7	-8	227	230	-17	-1	3	2	7	-11	49	53	-50
10	50	47	29	-6	212	211	6	1	217	206	61	-9	16	14	17
				-4	134	134	-3	3	2	5	-17	-7	180	183	-16
h 2 4				-2	152	155	-21	5	197	201	-21	-5	32	32	10
				0	18	20	-21	7	131	131	0	-3	184	185	-1
-12	35	31	47	2	14	14	-1	9	163	162	8	-1	86	85	4
-10	34	33	6	4	56	54	16	11	59	56	36	1	105	105	-5
-8	197	192	28	6	29	26	28					3	2	1	1
-6	186	177	59					h 3 3				5	15	15	-1
-4	518	486	75	h 2 10											
-2	124	123	5					-11	100	99	6	h 3 9			
0	20	16	74	-12	104	98	51	-9	183	182	4				
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6	105	100	45	-6	70	70	-5	-3	429	419	30	-7	60	56	51
8	142	140	12	-4	107	105	17	-1	128	132	-42	-5	129	130	-11
10	127	128	-4	-2	223	220	16	1	77	76	8	-3	218	220	-11
				0	24	28	-53	3	157	152	36	-1	117	116	9
h 2 5				2	193	197	-23	5	72	66	68	1	127	135	-75
				4	91	87	31	7	9	6	17	3	205	204	4
-12	21	26	-62					9	19	19	-2	5	106	97	80
-10	96	103	-67	h 2 11											
-8	66	68	-25					h 3 4				h 3 10			
-6	23	25	-34	-10	25	28	-38								
-4	163	156	54	-8	161	161	1	-11	6	2	13	-9	44	48	-52
-2	159	149	69	-6	7	2	18	-9	111	115	-40	-7	170	173	-22
0	271	257	65	-4	162	161	4	-7	188	182	36	-5	18	21	-31
2	11	17	-91	-2	78	83	-62	-5	164	167	-23	-3	78	81	-26
4	327	323	12	0	-6	0	-17	-3	211	192	104	-1	24	28	-48
6	22	22	0	2	64	63	12	-1	174	164	64	1	57	56	9
8	133	129	29					1	129	119	86	3	4	2	4
10	82	81	8	h 2 12				3	123	120	25				
								5	142	138	31	h 3 11			
h 2 6				-10	23	19	30	7	108	107	14				
				-8	88	86	15	9	60	57	32	-9	-7	0	-20
-12	149	144	37	-6	181	179	7					-7	26	24	22
-10	138	137	5	-4	71	71	0	h 3 5				-5	52	48	41
-8	27	24	42	-2	42	49	-94					-3	49	44	63
-6	61	62	-22	0	24	30	-68	-11	116	114	17	-1	92	89	32
-4	407	409	-4					-9	230	236	-30	1	75	80	-63
-2	416	411	15	h 2 13				-7	278	284	-23				
0	48	47	14					-5	83	81	21	h 3 12			
2	165	166	-2	-8	28	27	5	-3	437	432	15				
4	249	248	2	-6	-7	6	-31	-1	453	448	13	-7	94	92	14
6	181	186	-29	-4	21	25	-43	1	168	171	-20	-5	-8	2	-29
8	54	51	41	-2	1	4	-4	3	82	82	2	-3	35	34	8
								5	128	130	-16	-1	78	77	10
h 2 7				h 3 0				7	58	61	-41				
								9	26	25	10	h 4 0			
-12	38	36	29	1	73	67	79								
-10	106	108	-26	3	68	64	54	h 3 6				0	205	207	-11

2	199	195	22
4	113	115	-20
6	123	125	-10
8	209	207	7
10	88	91	-32

h 4 1

-10	87	86	12
-8	80	78	28
-6	347	346	1
-4	110	111	-15
-2	211	205	31
0	320	314	19
2	151	149	21
4	216	217	-8
6	193	196	-18
8	142	144	-14
10	76	75	8

h 4 2

-10	72	71	3
-8	51	51	9
-6	86	86	3
-4	44	48	-62
-2	88	90	-26
0	190	191	-7
2	82	85	-41
4	27	27	3
6	1	3	-4
8	39	36	36
10	13	18	-42

h 4 3

-10	50	49	12
-8	133	137	-32
-6	6	3	12
-4	201	195	38
-2	109	110	-12
0	138	135	24
2	74	72	21
4	161	165	-29
6	53	53	0
8	60	61	-10

h 4 4

-10	39	36	31
-8	68	72	-56
-6	31	29	23
-4	7	3	14
-2	49	50	-23
0	99	102	-33
2	-4	2	-12
4	101	105	-34
6	132	132	-1
8	59	56	39

h 4 5

-10	10	5	20
-8	37	39	-28
-6	149	141	61
-4	94	101	-81
-2	241	235	31
0	97	105	-85
2	133	133	0
4	51	55	-57
6	29	29	-3
8	43	39	39

h 4 6

1	79	82	-33

-10	100	102	-12
-8	126	136	-87
-6	11	8	21
-4	238	236	10
-2	247	245	10
0	78	75	39
2	86	84	20
4	110	108	10
6	67	70	-43

h 4 7

-10	33	34	-10
-8	5	10	-22
-6	39	45	-85
-4	258	266	-35
-2	35	31	54
0	331	335	-15
2	183	181	6
4	24	28	-40
6	88	90	-15

h 4 8

-10	92	88	41
-8	39	39	7
-6	121	113	67
-4	89	87	16
-2	35	37	-23
0	20	14	49
2	10	3	31
4	33	30	30

h 4 9

-8	10	13	-14
-6	8	9	-4
-4	56	61	-71
-2	137	137	5
0	148	148	3
2	23	17	55

h 4 10

-8	45	43	30
-6	57	56	1
-4	6	13	-50
-2	49	44	61
0	39	39	5
2	22	27	-63

h 4 11

-6	9	8	3
-4	-3	7	-25
-2	21	20	10

h 5 0

1	-3	1	-6
3	15	14	7
5	125	124	8
7	7	6	4
9	129	127	16

h 5 1

-9	4	1	7
-7	75	75	-2
-5	67	73	-71
-3	161	162	-8
-1	19	22	-44
1	79	82	-33

3	36	36	-8
5	49	46	40
7	40	39	12

h 5 2

-9	25	23	22
-7	100	101	-8
-5	41	39	28
-3	27	27	3
-1	13	9	29
1	101	97	38
3	38	39	-9
5	67	67	-3
7	61	58	35

h 5 3

-9	26	25	3
-7	66	68	-25
-5	181	189	-56
-3	10	8	12
-1	358	356	8
1	349	350	-2
3	30	24	62
5	215	217	-7
7	232	224	42

h 5 4

-9	21	15	47
-7	49	47	20
-5	118	115	24
-3	32	29	40
-1	69	69	0
1	47	49	-24
3	52	51	13
5	74	72	20
7	25	21	48

h 5 5

-9	64	71	-89
-7	58	55	45
-5	182	186	-24
-3	46	50	-48
-1	135	133	11
1	115	114	1
3	11	16	-46
5	126	124	10

h 5 6

-9	-1	4	-6
-7	42	42	0
-5	32	34	-23
-3	176	174	13
-1	10	6	19
1	98	101	-22
3	14	16	-11
5	7	4	11

h 5 7

-7	13	13	-6
-5	9	1	29
-3	13	8	31
-1	8	7	3
1	50	52	-25
3	75	72	32

h 5 8

-7	49	46	38

-5	26	30	-57
-3	35	39	-43
-1	110	111	-11
1	53	55	-21

h 5 9

-5	115	108	63
-3	35	35	2
-1	3	1	3

h 6 0

0	82	83	-7
2	124	121	25
4	52	49	35
6	125	123	22

h 6 1

-6	27	30	-27
-4	21	15	56
-2	144	141	21
0	166	167	-6
2	20	17	31
4	91	91	0
6	83	80	32

h 6 2

-6	10	7	16
-4	134	133	6
-2	10	3	31
0	136	137	-5
2	46	45	14
4	32	32	-10

h 6 3

-6	24	24	0
-4	6	9	-13
-2	62	58	53
0	6	8	-7
2	55	55	0
4	15	15	2

h 6 4

-6	48	52	-55
-4	129	126	25
-2	56	60	-52
0	130	133	-21
2	20	19	6
4	90	92	-12

h 6 5

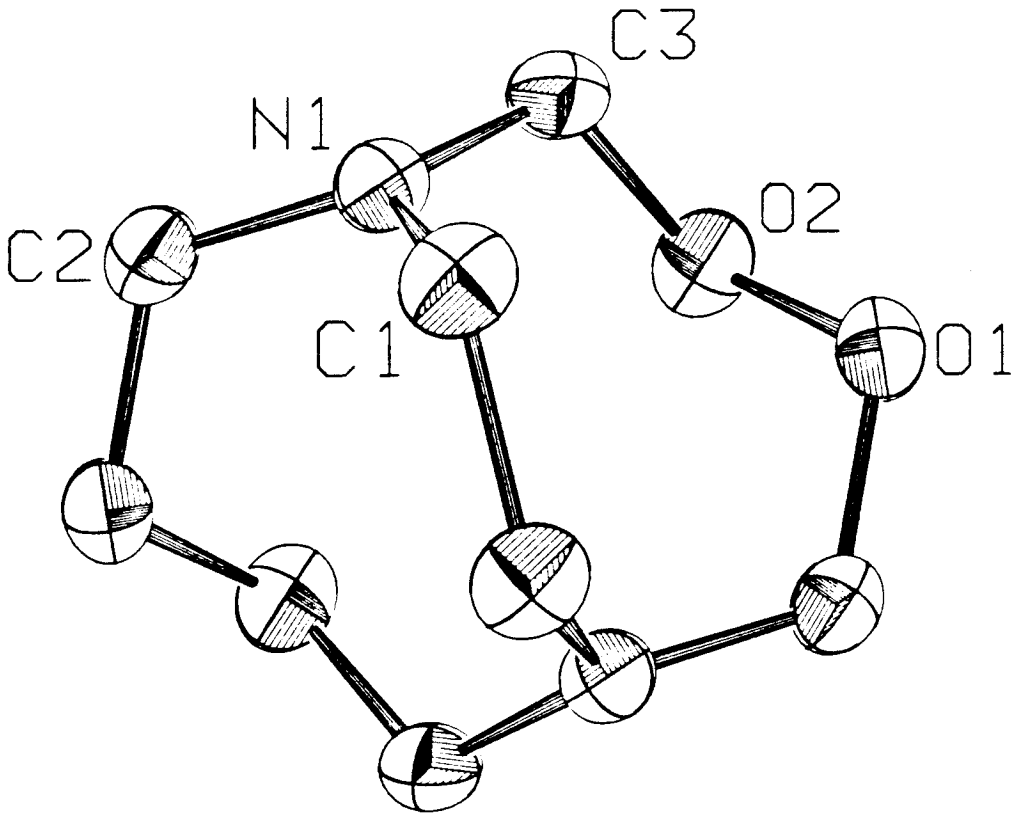
-6	33	34	-17
-4	10	17	-62
-2	51	49	28
0	40	41	-4
2	82	81	8

h 6 6

-4	94	94	0
-2	81	82	-13
0	62	60	19

h 6 7

-2	24	25	-4



An ORTEP drawing of HMDD.

Figure III-9

Table III-22 compares average bond lengths, angles, torsion angles, and out-of-plane distances among HMTD, BTDD, CTDD, HMDD, the tricyclotetradecane, and "normal" values. The most striking thing that this table makes apparent is that the C-N-C angles of HMTD, BTDD, CTDD, and HMDD are all 120° within two esd's. Furthermore, the out-of-plane distances for BTDD, CTDD, and HMDD are all 0.13-0.14Å, much smaller than would be otherwise expected. This is a strong argument that the planarity about the bridgehead nitrogen atoms in HMTD (and the near planarity in the other three compounds) is intimately associated with the peroxide groups. Further inspection of the data for these four compounds shows that the O-O distances are all short (suggesting that electron density is being withdrawn from the peroxides), all of the N-C bonds are of approximately the same length (and all very short), and the N-C-O and C-O-O angles are all quite similar. The only major differences arise in the C-O bond distances and the C-O-O-C torsion angle. As stated above, it takes little energy, as far as the C-O-O-C groups are concerned, to rotate about the O-O bond. Furthermore, the torsion angles in BTDD, CTDD, and HMDD are very close to one another. With this in mind, one might postulate that the differences in this torsion angle are due to the length of the third bridge. In order to better investigate this theory, compounds with different bridge lengths must be synthesized and studied. Meanwhile, the question of the differences in C-O bond lengths remains to be answered.

Table III-22

Important Average Distances (Å) and Angles (°)

in Several Compounds.

	HMTD	BTDD	CTDD	HMDD	TCTD	Normal
O-O	1.456(8)	1.464(10)	1.455(4)	1.465(1)	1.472(1)	1.479(2)
C-O	1.421(9)	1.452(17)	1.440(5)	1.437(1)	1.437(1)	1.432(3)
N-C	1.421(8)	1.424(4)	1.412(5)	1.416(1)	1.447(1)	—
C-N-C	120.0(5)	120.2(2)	120.0(3)	120.2(1)	—	108
N-C-O	116.2(5)	115.1(6)	116.7(3)	116.6(1)	113.5(1)	—
C-O-O	106.3(5)	105.1(12)	106.4(2)	106.2(1)	107.6(1)	107.8(3)
C-O-O-C	129.3(5)	115.8(4)	114.7(3)	115.4(1)		—
Distance out of plane	0.0	0.13	0.14	0.13	—	0.52

The C-O bond lengths in BTDD, CTDD, and HMDD are slightly longer than "expected" from other organic peroxides (the bond length in BTDD is apparently much longer than expected, although the uncertainty in this length is also rather large). In CTDD, HMDD, and the tricyclotetradecane, however, this difference is only on the order of a two-hundredth of an angstrom. Although the anomeric effect creates no "standard" amount of bond lengthening, 0.005Å is too small of a difference in length to make the anomeric effect alone a credible explanation for the strange geometries observed in BTDD, CTDD, and HMDD. Nevertheless, these lengthenings do suggest that the anomeric effect perhaps should be invoked as one factor in any explanation of this phenomenon.

The structures of BTDD, CTDD, and HMDD do make one thing certain: the geometry observed in HMTD does not arise out of any kind of accident or coincidence. The C-N-C bond angles between peroxide bridges are invariably 120°, and the same bond lengths (with the exception of C-O) are short in these molecules and HMTD. Thus, the remaining structural puzzle is determining to what degree steric and electronic effects influence the geometry of these molecules.

CHAPTER IV. MM2 and MNDO Models

A. Introduction

One way to investigate steric and electronic effects in relatively simple molecules is through computer simulations. Steric effects and the like may be investigated with a purely classical force-field approach, whereas reasonable studies of electronic effects need to take molecular orbitals into consideration. One first attempts to make a classical model, and if this model is not accurate then quantum-mechanical (or semi-quantum-mechanical) methods may be applied.

Classical molecular mechanics programs look at molecules as sets of space-filling "balls" (atoms) which are connected with "springs". By adjusting the parameters for these "springs", one can specify desired bond lengths, angles, and torsion angles all with their accompanying force constants). Furthermore, electrostatic and non-bonded interactions are taken into consideration. The programs calculate total steric energies for the molecule, and then set about changing configurations in such a way as to minimize this total energy.

Quantum-mechanical molecular modeling programs work in a similar manner, in that the total energy is minimized in order to find a preferred conformation. The major difference is in the method used to minimize the energy; these programs calculate molecular orbitals and use these for the minimization procedure. Theoretically, a much more complete model of a molecule can be

fashioned in this way. One major drawback with this method, however, is that it can be very difficult to understand why certain effects arise. In cases such as this, it is helpful to simulate similar compounds also; with luck, the differences between the known properties and the calculated properties of the molecule being studied and the similar molecules can make evident just what types of electronic effects are coming into play and what they are doing to the molecular conformations.

B. MM2

HMTD was modeled using a molecular mechanics program, MM2[40,41]. The program's standard bond lengths and force constants were used where available. In addition, parameters were added for O-O and N-C bonds. For the O-O bonds, a R_o of 1.47A and a K_s of 7.81 were used. For the N-C bonds, a R_o of 1.45A and a K_s of 5.1 were used. Standard parameters were also used for bond angle and bending and stretch-bend energy calculations, with the exception of the C-N-C, N-C-O, and C-O-O bond angles. The parameters for these were: C-N-C, θ_o=107.7°, KB=0.63, KSB=0.12; N-C-O, θ_o=110.0°, KB=0.45, KSB=0.12; C-O-O, θ_o=104.0°, KB=0.62, KSB=0.12.

The program ran through sixteen iterations, for a final total energy of 34.48(1) kcal/mol. Of this energy, 1.31 kcal/mol arises from compression, 10.53 kcal/mol from bending, 0.91 kcal/mol from stretch-bend, 15.69 kcal/mol from 1,4 Van der Waals, -2.64 kcal/mol from other Van der Waals, 2.97 kcal/mol from torsion, and 5.70 kcal/mol from dipole interactions. The final atomic coordinates are given in Table IV-1, the bond lengths and stretching energies in Table IV-2, the non-bonded distances and Van der Waals energies in Table IV-3, and the bond angles and bending and stretch-bend energies in Table IV-4.

As the Tables show, MM2 predicted a geometry for HMTD that is rather different from the observed geometry. The C-N-C bond angles predicted by MM2 average to 116°, and the bridgehead nitrogen atoms are 0.29Å and 0.30Å out of the respective carbon planes. Bond lengths were increased, if anything (although this

is not unexpected--there are few purely mechanical forces which would shorten a bond). The program predicts that instead of being planar or out-out, the bridgehead nitrogen atoms prefer the in,in configuration despite a 1.39 Kcal/mole non-bonded interaction between them.

These MM2 results would seem to imply that there are electronic effects involved in the HMTD geometry. One must be a bit cautious about this conclusion, however. The equilibrium bond lengths used for the peroxide bonds may have been large, for instance (as the studies of organic peroxides mentioned above would seem to indicate). If the equilibrium bond length parameters for these bonds were to be made smaller, it is quite conceivable that MM2 would predict the observed geometry; shorter bonds would bring the bridgehead nitrogen atoms even closer together, and it is likely that they would move toward planarity to avoid a strong positive Van der Waals interaction. Whether or not MM2 would then predict that they should favor the out,out conformation in this case is not known.

One can still make a strong argument that there is at least some validity in these MM2 results; after all, if it is hard to postulate mechanical forces that would shorten a bond, then there are probably some electronic forces involved in this shortening. MM2 showed that the electronic forces which shorten bond lengths in the molecule are also involved in determining the molecular geometry. Thus, quantitative molecular mechanics calculations were called for to help resolve this problem.

Table IV-1

FINAL ATOMIC COORDINATES

ATOM	X	Y	Z
N(1)	0.00166	0.11691	1.28797
C(2)	1.21588	0.92767	1.39378
O(3)	1.30795	1.92696	0.38667
O(4)	1.83609	1.36132	-0.88243
C(5)	0.76516	1.02223	-1.75291
N(6)	0.03672	-0.14150	-1.26077
C(7)	-1.38880	-0.20539	-1.58667
O(8)	-2.18943	-0.13672	-0.41350
O(9)	-1.90641	1.12863	0.31114
C(10)	-1.25294	0.82607	1.53812
C(11)	0.08717	-1.24887	1.79512
O(12)	0.94535	-2.04249	0.98515
O(13)	0.31742	-2.33284	-0.33101
C(14)	0.76058	-1.41168	-1.32102
H(15)	1.24581	1.42990	2.39010
H(16)	2.12858	0.28972	1.32665
LP(17)	1.75493	2.29141	0.56119
LP(18)	0.74127	2.06198	0.24939
LP(19)	2.11080	1.83330	-1.13762
LP(20)	2.06875	0.83870	-0.70891
H(21)	1.18009	0.81220	-2.76746
H(22)	0.10347	1.91844	-1.82244
H(23)	-1.69826	0.62428	-2.26574
H(24)	-1.63966	-1.16164	-2.10371
LP(25)	-1.96229	-0.54904	-0.04341
LP(26)	-2.75765	-0.06729	-0.60121
LP(27)	-1.48774	1.38241	-0.03383
LP(28)	-2.45387	1.33307	0.45745
H(29)	-1.07334	1.79120	2.06808
H(30)	-1.95441	0.22889	2.16793
H(31)	0.48370	-1.24257	2.83828
H(32)	-0.91174	-1.74671	1.79839
LP(33)	0.96199	-2.58432	1.24874
LP(34)	1.39918	-1.68203	0.83871
LP(35)	0.56566	-2.86145	-0.47944
LP(36)	-0.25818	-2.19745	-0.23817
H(37)	1.85673	-1.25856	-1.18078
H(38)	0.61969	-1.87892	-2.32482

Table IV-2

BOND LENGTHS AND STRETCHING ENERGY (39 BONDS)

ENERGY = 71.94(KS)(DR)(DR)(1+(CS)(DR))
DR = R-R0
CS = -2.000

BOND	LENGTH	R(0)	K(S)	ENERGY
N(1)- C(2)	1.4638	1.4500	5.1000	0.0683
N(1)- C(10)	1.4627	1.4500	5.1000	0.0578
N(1)- C(11)	1.4594	1.4500	5.1000	0.0318
C(2)- O(3)	1.4217	1.4070	5.3600	0.0813
C(2)- H(15)	1.1161	1.1130	4.6000	0.0032
C(2)- H(16)	1.1156	1.1130	4.6000	0.0022
O(3)- O(4)	1.4864	1.4700	7.8100	0.1468
O(3)-LP(17)	0.6026	0.6000	4.6000	0.0001
O(3)-LP(18)	0.5985	0.6000	4.6000	0.0008
O(4)- C(5)	1.4211	1.4070	5.3600	0.0748
O(4)-LP(19)	0.6026	0.6000	4.6000	0.0026
O(4)-LP(20)	0.5978	0.6000	4.6000	0.0016
C(5)- N(6)	1.4585	1.4500	5.1000	0.0258
C(5)- H(21)	1.1161	1.1130	4.6000	0.0031
C(5)- H(22)	1.1162	1.1130	4.6000	0.0033
N(6)- C(7)	1.4637	1.4500	5.1000	0.0668
N(6)- C(14)	1.4632	1.4500	5.1000	0.0623
C(7)- O(8)	1.4220	1.4070	5.3600	0.0540
C(7)- H(23)	1.1159	1.1130	4.6000	0.0028
C(7)- H(24)	1.1157	1.1130	4.6000	0.0023
O(8)- O(9)	1.4834	1.4700	7.8100	0.1286
O(8)-LP(25)	0.5988	0.6000	4.6000	0.0005
O(8)-LP(26)	0.6024	0.6000	4.6000	0.0020
O(9)- C(10)	1.4227	1.4070	5.3600	0.0919
O(9)-LP(27)	0.5989	0.6000	4.6000	0.0004
O(9)-LP(28)	0.6024	0.6000	4.6000	0.0019
C(10)- H(29)	1.1156	1.1130	4.6000	0.0022
C(10)- H(30)	1.1160	1.1130	4.6000	0.0029
C(11)- O(12)	1.4221	1.4070	5.3600	0.0852
C(11)- H(31)	1.1160	1.1130	4.6000	0.0030
C(11)- H(32)	1.1161	1.1130	4.6000	0.0032
O(12)- O(13)	1.4849	1.4700	7.8100	0.1551
O(12)-LP(33)	0.6028	0.6000	4.6000	0.0025
O(12)-LP(34)	0.5979	0.6000	4.6000	0.0016
O(13)- C(14)	1.4230	1.4070	5.3600	0.0960
O(13)-LP(35)	0.6024	0.6000	4.6000	0.0022
O(13)-LP(36)	0.5986	0.6000	4.6000	0.0007
C(14)- H(37)	1.1156	1.1130	4.6000	0.0021
C(14)- H(38)	1.1161	1.1130	4.6000	0.0033

Table IV-3

NON-BONDED DISTANCES, VAN DER WAALS ENERGY
586 VDW INTERACTIONS (1,3 EXCLUDED)

ENERGY = KV*(2.90(10**5)EXP(-12.50/P) - 2.25(P**6))
RV = RVDW(I) + RVDW(K)
KV = SQRT(EPS(I)*EPS(K))
P = (RV/R) OR (RV/R#)
(IF P.GT.3.311, ENERGY = KV(336.176)(P**2))

IN THE VDW CALCULATIONS THE HYDROGEN ATOMS ARE RELOCATED SO THAT THE ATTACHED HYDROGEN DISTANCE IS REDUCED BY 0.915

* * INTERACTIONS OF LESS THAN 0.1 KCAL ARE NOT PRINTED * *

ATOM PAIR	R	R#	RV	KV	ENERGY	(1,4)
N(1), N(5)	2.5621		3.640	0.0550	1.3907	
N(1), O(8)	2.7857		3.560	0.0524	0.3458	*
N(1), O(13)	2.9533		3.560	0.0524	0.1150	*
N(1),LP(18)	2.3257		3.020	0.0297	0.2475	*
N(1),LP(27)	2.3594		3.020	0.0297	0.2001	*
N(1),LP(34)	2.3219		3.020	0.0297	0.2535	*
C(2), N(5)	3.0952		3.720	0.0492	0.1003	
C(2), O(13)	3.0103		3.640	0.0469	0.1107	*
C(2),LP(20)	2.2708		3.100	0.0265	0.4256	*
C(2), H(29)	2.5379	2.5134	3.340	0.0460	0.5264	*
C(2), H(31)	2.7079	2.6715	3.340	0.0460	0.2115	*
O(3), N(5)	2.9340		3.560	0.0524	0.1339	*
O(3), C(10)	3.0160		3.640	0.0469	0.1060	*
O(3), H(22)	2.5161	2.4089	3.240	0.0485	0.4264	*
O(4), C(14)	3.0054		3.640	0.0469	0.1141	*
O(4), H(15)	2.4736	2.4467	3.240	0.0485	0.5297	*
O(4), H(37)	2.6309	2.4931	3.240	0.0485	0.1435	
C(5),LP(15)	2.2563		3.100	0.0265	0.4574	*
C(5), H(23)	2.5475	2.5231	3.340	0.0460	0.5074	*
C(5), H(37)	2.5985	2.5536	3.340	0.0460	0.4034	*
N(6), O(9)	2.8035		3.560	0.0524	0.3124	*
N(6),LP(30)	2.3226		3.020	0.0297	0.2523	*
N(6),LP(33)	2.3757		3.020	0.0297	0.1795	*
N(6),LP(36)	2.3151		3.020	0.0297	0.2643	*
C(7), O(13)	3.0023		3.640	0.0469	0.1177	*
C(7), H(22)	2.6024	2.5775	3.340	0.0460	0.3725	*
C(7),LP(27)	2.2231		3.100	0.0265	0.5453	*
C(7), H(36)	2.7165	2.6791	3.340	0.0460	0.2011	*
O(8), H(30)	2.6178	2.5738	3.240	0.0485	0.2425	*
O(9), H(23)	2.6340	2.5745	3.240	0.0485	0.2134	*
C(10), H(15)	2.7082	2.6711	3.340	0.0460	0.2121	*
C(10),LP(25)	2.2125		3.100	0.0265	0.5754	*
C(10), H(32)	2.6283	2.5792	3.340	0.0460	0.3690	*

Table IV-3 (continued)

ATOM PAIR	R	R#	RV	KV	ENERGY	(1,4)
C(11), H(16)	2.5465	2.5726	3.340	0.0450	0.3873	*
C(11), H(30)	2.5477	2.5218	3.340	0.0450	0.5095	*
C(11),LP(35)	2.2701		3.100	0.0265	0.4878	*
C(12), H(16)	2.6374	2.6589	3.340	0.0450	0.1481	
C(12), H(37)	2.4778	2.4529	3.340	0.0450	0.5179	*
C(13), H(32)	2.5676	2.4975	3.340	0.0450	0.3991	*
C(14), H(31)	2.6359	2.6501	3.340	0.0450	0.2429	*
C(14), H(34)	2.5370	2.5129	3.340	0.0450	0.5278	*
C(14),LP(34)	2.2683		3.100	0.0265	0.4318	*
H(15),LP(17)	2.0848	2.0302	2.700	0.0274	0.3171	*
H(15), H(37)	2.3691	2.3709	3.000	0.0470	0.2545	
H(16),LP(17)	2.1754	2.1154	2.700	0.0274	0.1771	*
H(16),LP(20)	2.1091	2.1004	2.700	0.0274	0.1973	
H(16),LP(34)	2.1582	2.1847	2.700	0.0274	0.1021	
LP(17),LP(19)	1.7951		2.400	0.0160	0.1981	*
LP(18), H(22)	2.1725	2.1574	2.700	0.0274	0.1283	
LP(19), H(21)	2.1366	2.0790	2.700	0.0274	0.2292	*
LP(19), H(22)	2.1226	2.0658	2.700	0.0274	0.2508	*
LP(20), H(21)	2.2423	2.1750	2.700	0.0274	0.1082	*
LP(20), H(37)	2.1601	2.1864	2.700	0.0274	0.1007	
H(22), H(23)	2.2622	2.2734	3.000	0.0470	0.4902	
H(23),LP(25)	2.0907	2.0362	2.700	0.0274	0.3050	*
H(24),LP(25)	2.1735	2.1134	2.700	0.0274	0.1798	*
H(24),LP(26)	2.1691	2.1099	2.700	0.0274	0.1843	*
H(24), H(38)	2.3808	2.3313	3.000	0.0470	0.2461	
LP(26),LP(28)	1.7816		2.400	0.0160	0.2180	*
LP(27), H(29)	2.1810	2.1806	2.700	0.0274	0.1705	*
LP(28), H(29)	2.1702	2.1110	2.700	0.0274	0.1828	*
LP(28), H(30)	2.0963	2.0415	2.700	0.0274	0.2947	*
H(30), H(32)	2.2642	2.2753	3.000	0.0470	0.4848	
H(31),LP(33)	2.1344	2.0769	2.700	0.0274	0.2326	*
H(31),LP(34)	2.2427	2.1783	2.700	0.0274	0.1079	*
H(32),LP(33)	2.1247	2.0678	2.700	0.0274	0.2474	*
H(32),LP(36)	2.1658	2.1709	2.700	0.0274	0.1149	
LP(33),LP(35)	1.7946		2.400	0.0160	0.1989	*
LP(34), H(37)	2.1135	2.1042	2.700	0.0274	0.1920	
LP(35), H(37)	2.1744	2.1146	2.700	0.0274	0.1732	*
LP(35), H(38)	2.0713	2.0365	2.700	0.0274	0.3046	*

Table IV-4

BOND ANGLES, BENDING AND STRETCH-BEND ENERGIES (78 ANGLES)

EB = 0.0E1914(KB)(DT)(DT)(1+SF*DT**4)
DT = THETA-TZERO
SF = 0.00700E-5

ESB(J) = 2.51124(KSB(J))(DT)(DR1+DR2)
DR(I) = R(I) - R0(I)
KSB(1) = 0.120 X-F-Y F = 1ST ROW ATOM
KSB(2) = 0.250 X-S-Y S = 2ND ROW ATOM
KSB(3) = 0.090 X-F-H (DR2 = 0)
KSB(4) =-0.400 X-S-H (DR2 = 0)
(X,Y = F OR S)

A T O M S	THETA	TZERO	KB	EB	KSB	ESB
C(2)- N(1)- C(10)	115.504	107.700	0.630	0.8411	0.12	0.0584
C(2)- N(1)- C(11)	116.398	107.700	0.630	1.0449	0.12	0.0709
C(10)- N(1)- C(11)	116.395	107.700	0.630	1.0441	0.12	0.0579
N(1)- C(2)- O(3)	113.066	110.000	0.450	0.0927	0.12	0.0764
N(1)- C(2)- H(15)	109.633	108.800	0.500	0.0076	0.09	0.0036
N(1)- C(2)- H(16)	110.950	108.800	0.500	0.0506	0.09	0.0047
O(3)- C(2)- H(15)	109.319	106.700	0.540	0.0310	0.09	0.0054
O(3)- C(2)- H(16)	107.838	106.700	0.540	0.0153	0.09	0.0038
H(15)- C(2)- H(16)	106.804	109.400	0.320	0.0473		
C(2)- O(3)- O(4)	111.121	104.000	0.620	0.6291	0.12	0.0669
C(2)- O(3)-LP(17)	105.545	105.160	0.350	0.0011		
C(2)- O(3)-LP(18)	105.054	105.160	0.350	0.0001		
O(4)- O(3)-LP(17)	102.350	103.260	0.350	0.0064		
O(4)- O(3)-LP(18)	103.086	103.260	0.350	0.0002		
LP(17)- O(3)-LP(18)	129.224	131.000	0.240	0.0166		
O(3)- O(4)- C(5)	110.244	104.000	0.620	0.5298	0.12	0.0575
O(3)- O(4)-LP(19)	103.028	103.260	0.350	0.0004		
O(3)- O(4)-LP(20)	102.894	103.260	0.350	0.0010		
C(5)- O(4)-LP(19)	105.720	105.160	0.350	0.0024		
C(5)- O(4)-LP(20)	105.213	105.160	0.350	0.0000		
LP(19)- O(4)-LP(20)	127.051	131.000	0.240	0.0200		
O(4)- C(5)- N(6)	111.105	110.000	0.450	0.0120	0.12	0.0075
O(4)- C(5)- H(21)	108.757	106.700	0.540	0.0501	0.09	0.0066
O(4)- C(5)- H(22)	107.056	106.700	0.540	0.0015	0.09	0.0011
N(6)- C(5)- H(21)	110.016	108.800	0.500	0.0162	0.09	0.0023
N(6)- C(5)- H(22)	111.444	108.800	0.500	0.0766	0.09	0.0051
H(21)- C(5)- H(22)	108.353	109.400	0.320	0.0077		
C(5)- N(6)- C(7)	116.496	107.700	0.630	1.0686	0.12	0.0587
C(5)- N(6)- C(14)	115.574	107.700	0.630	0.8562	0.12	0.0514
C(7)- N(6)- C(14)	115.749	107.700	0.630	0.8992	0.12	0.0654
N(6)- C(7)- O(8)	111.257	110.000	0.450	0.0156	0.12	0.0109
N(6)- C(7)- H(23)	111.908	108.800	0.500	0.1059	0.09	0.0096
N(6)- C(7)- H(24)	111.075	108.800	0.500	0.0567	0.09	0.0070
O(8)- C(7)- H(23)	108.060	106.700	0.540	0.0219	0.09	0.0046
O(8)- C(7)- H(24)	107.286	106.700	0.540	0.0041	0.09	0.0020

Table IV-4 (continued)

ATOMS	THETA	THEO	KR	EE	KSE	EIE
H(23)- C(7)- H(24)	107.031	109.400	0.320	0.0394		
C(7)- O(8)- O(9)	109.654	104.000	0.620	0.4244	0.12	0.0517
C(7)- O(8)-LP(25)	105.252	105.160	0.350	0.0001		
C(7)- O(8)-LP(26)	106.234	105.160	0.350	0.0088		
O(9)- O(8)-LP(25)	102.286	103.260	0.350	0.0073		
O(9)- O(8)-LP(26)	103.506	103.260	0.350	0.0005		
LP(25)- O(8)-LP(26)	127.035	131.000	0.240	0.0204		
O(8)- O(9)- C(10)	109.093	104.000	0.620	0.3524	0.12	0.0477
O(8)- O(9)-LP(27)	102.305	103.260	0.350	0.0069		
O(8)- O(9)-LP(28)	103.557	103.260	0.350	0.0007		
C(10)- O(9)-LP(27)	105.414	105.160	0.350	0.0005		
C(10)- O(9)-LP(28)	106.267	105.160	0.350	0.0094		
LP(27)- O(9)-LP(28)	129.151	131.000	0.240	0.0180		
N(1)- C(10)- O(9)	110.462	110.000	0.450	0.0021	0.12	0.0040
N(1)- C(10)- H(29)	111.259	108.800	0.500	0.0662	0.09	0.0071
N(1)- C(10)- H(30)	113.100	108.800	0.500	0.1193	0.09	0.0095
O(9)- C(10)- H(29)	107.437	106.700	0.540	0.0064	0.09	0.0026
O(9)- C(10)- H(30)	103.169	106.700	0.540	0.0255	0.09	0.0052
H(29)- C(10)- H(30)	107.230	109.400	0.320	0.0333		
N(1)- C(11)- O(12)	111.052	110.000	0.450	0.0115	0.12	0.0080
N(1)- C(11)- H(31)	109.899	108.800	0.500	0.0132	0.09	0.0023
N(1)- C(11)- H(32)	111.470	108.800	0.500	0.0781	0.09	0.0057
O(12)- C(11)- H(31)	108.730	106.700	0.540	0.0488	0.09	0.0069
O(12)- C(11)- H(32)	107.028	106.700	0.540	0.0013	0.09	0.0011
H(31)- C(11)- H(32)	108.529	109.400	0.320	0.0053		
C(11)- O(12)- O(13)	110.995	104.000	0.620	0.6647	0.12	0.0674
C(11)- O(12)-LP(33)	105.619	105.160	0.350	0.0016		
C(11)- O(12)-LP(34)	105.139	105.160	0.350	0.0000		
O(13)- O(12)-LP(33)	102.393	103.260	0.350	0.0010		
O(13)- O(12)-LP(34)	102.798	103.260	0.350	0.0016		
LP(33)- O(12)-LP(34)	128.918	131.000	0.240	0.0228		
O(12)- O(13)- C(14)	110.971	104.000	0.620	0.6604	0.12	0.0692
O(12)- O(13)-LP(35)	102.437	103.260	0.350	0.0052		
O(12)- O(13)-LP(36)	102.982	103.260	0.350	0.0006		
C(14)- O(13)-LP(35)	105.557	105.160	0.350	0.0012		
C(14)- O(13)-LP(36)	105.127	105.160	0.350	0.0000		
LP(35)- O(13)-LP(36)	129.259	131.000	0.240	0.0159		
N(6)- C(14)- O(13)	112.286	110.000	0.450	0.0515	0.12	0.0201
N(6)- C(14)- H(37)	111.209	108.800	0.500	0.0635	0.09	0.0072
N(6)- C(14)- H(38)	109.754	108.800	0.500	0.0100	0.09	0.0028
O(13)- C(14)- H(37)	107.901	106.700	0.540	0.0171	0.09	0.0044
O(13)- C(14)- H(38)	108.384	106.700	0.540	0.0336	0.09	0.0061
H(37)- C(14)- H(38)	107.129	109.400	0.320	0.0362		

B. MNDO

i. Introduction

Semi-quantitative molecular orbital calculations were performed using the program MNDO[42]. In order to better understand the results of this program for HMTD, calculations were first performed on several test compounds: methyl amine, hydroperoxymethylamine, di(hydroperoxymethyl)amine, and tri(hydroperoxymethyl)amine (where the hydroperoxymethyl group is $-CH_2OOH$). Following are the results of these calculations.

ii. Methylamine

The final data from the methylamine calculations is given in Tables IV-5 through IV-7. The Tables contain, respectively, final atomic parameters, final bond lengths, and final bond angles.

Table IV-5

Final MNDO Atomic Parameters for Methylamine.

atom	x	y	z
N1	1.00847	0.0	0.0
C1	1.50563	-0.65316	1.20809
H1	0.0	0.0	0.0
H2	1.27945	0.97114	0.0
H3	1.15680	-0.18025	2.15840
H4	2.61842	-0.62797	1.21212
H5	1.18037	-1.71730	1.21794

Table IV-6

Final MNDO Bond Lengths (Å) for Methylamine

H1-N1	1.0085
H2-N1	1.0082
C1-N1	1.4606
C1-H3	1.1173
C1-H4	1.1131
C1-H5	1.1128

Table IV-7

Final MNDO Angles (°) for Methylamine

H2-N1-H1	105.59
C1-N1-H1	109.90
C1-N1-H2	109.83
H3-C1-N1	114.08
H4-C1-N1	109.46
H5-C1-N1	109.60
H4-C1-H3	107.43
H5-C1-H3	107.82
H5-C1-H4	108.29

iii. Hydroperoxymethylamine

The data for hydroperoxymethylamine calculations are given in Tables IV-8 through IV-10. The Tables contain, respectively, final atomic parameters, bond lengths, and bond angles.

Table IV-8

Final MNDO Atomic Parameters for Hydroperoxymethylamine

atom	X	Y	Z
N1	1.00754	0.0	0.0
C1	1.55101	-0.73062	1.14136
O1	1.01599	-0.29974	2.39570
O2	1.56570	0.76589	2.87906
H1	0.0	0.0	0.0
H2	1.29092	0.96631	0.0
H3	2.67158	-0.67932	1.10961
H4	1.24920	-1.81029	1.05934
H5	1.73277	0.61069	3.81454

Table IV-9

Final MNDO Bond Lengths (Å) for Hydroperoxymethylamine

N1-H1	1.0075
N1-H2	1.0070
N1-C1	1.4601
C1-O1	1.4301
C1-H3	1.1222
C1-H4	1.1241
O1-O2	1.2928
O2-H5	0.9629

Table IV-10

Final MNDO Bond Angles (°) for Hydroperoxymethylamine

H2-N1-H1	106.34
C1-N1-H1	111.85
C1-N1-H2	112.05
O1-C1-N1	113.30
H3-C1-N1	109.07
H4-C1-N1	108.88
H3-C1-O1	112.62
H4-C1-O1	104.65
H4-C1-H3	108.06
O2-O1-C1	114.66
H5-O2-O1	107.71
C1-O1-O2-H5	134.96

iv. Di(hydroperoxymethyl)amine

The data for di(hydroperoxymethyl)amine are given in Tables IV-11 through IV-13. The Tables contain, respectively, final atomic parameters, bond lengths, and bond angles.

Table IV-11

Final MNDO Atomic Parameters for Di(hydroperoxymethyl)amine

atom	x	y	z
N1	1.00618	0.0	0.0
C1	1.57098	1.34638	0.0
C2	1.56715	-1.10232	0.77289
O1	0.94365	-1.23783	2.05063
O2	1.54559	-0.63958	3.02427
O3	1.46655	2.01665	1.25237
O4	0.30587	2.53447	1.49218
H1	0.0	0.0	0.0
H2	2.68305	-1.01989	0.83155
H3	1.31951	-2.05861	0.23194
H4	1.62600	-1.26855	3.74959
H5	1.08884	1.92318	-0.83465
H6	2.67420	1.29620	-0.20558
H7	0.10614	2.38403	2.42184

Table IV-12

Final MNDO Bond Lengths (Å) for Di(hydroperoxymethyl)amine

N1-H1	1.0062
N1-C1	1.4600
N1-C2	1.4585
C1-O3	1.4243
C1-H5	1.1233
C1-H6	1.1233
C2-O1	1.4282
C2-H2	1.1205
C2-H3	1.1263
O1-O2	1.2916
O2-H4	0.9634
O3-O4	1.2934
O4-H7	0.9627

Table IV-13

Final MNDO Bond Angles (°) for Di(hydroperoxymethyl)amine

C1-N1-H1	112.76
C2-N1-H1	112.62
C1-N1-C2	123.24
O3-C1-N1	113.93
H5-C1-N1	107.91
H6-C1-N1	109.80
H5-C1-O3	112.35
H6-C1-O3	104.71
H6-C1-H5	107.97
O1-C2-N1	112.20
H2-C2-N1	110.81
H3-C2-N1	107.62
H2-C2-O1	113.26
H3-C2-O1	104.66
H3-C2-H2	107.85
O1-O2-C2	115.28
H4-O2-O1	107.70
O4-O3-C1	114.66
H7-O3-O4	107.62
C1-O3-O4-H7	140.10
C2-O1-O2-H4	131.36

V. Tri(hydroperoxymethyl)amine

The data for tri(hydroperoxymethyl)amine are given in Tables IV-14 through IV-16. The Tables contain, respectively, final atomic parameters, bond lengths, and bond angles.

Table IV-14

Final MNDO Atomic Parameters for Tri(hydroperoxymethyl)amine

atom	x	y	z
N1	1.46186	0.0	0.0
C1	0.0	0.0	0.0
C2	2.19050	1.27318	0.0
C3	2.19118	-1.26340	0.15257
O1	2.15361	-1.74384	1.49060
O2	3.13972	-1.37199	2.23608
O3	2.48959	1.69839	1.32654
O4	1.71725	2.61843	1.79665
O5	-0.52677	0.36348	1.27314
O6	-0.76215	-0.62323	2.07424
H1	3.23685	-1.15353	-0.23985
H2	1.68955	-2.06454	-0.45729
H3	2.77857	-0.99780	3.04660
H4	1.62707	2.03926	-0.59493
H5	3.18706	1.13953	-0.50307
H6	1.35876	2.31578	2.63808
H7	-1.64263	-0.49320	2.44327
H8	-0.39277	-0.98595	-0.36431
H9	-0.37841	0.78994	-0.70681

Table IV-15

Final MNDO Bond Lengths (Å) for Tri(hydroperoxymethyl)amine

N1-C1	1.4619
N1-C2	1.4669
N1-C3	1.4668
C1-O5	1.4250
C1-H8	1.1221
C1-H9	1.1255
C2-O3	1.4248
C2-H4	1.1217
C2-H5	1.1243
C3-O1	1.4222
C3-H1	1.1223
C3-H2	1.1249
O1-O2	1.2909
O2-H3	0.9630
O3-O4	1.2900
O4-H6	0.9634
O5-O6	1.2926
O6-H7	0.9635

Table IV-16

Final MNDO Bond Angles (°) for Tri(hydroperoxymethyl)amine

C1-N1-C2	119.78
C1-N1-C3	119.82
C2-N1-C3	120.04
N1-C1-O5	111.70
N1-C1-H8	110.49
N1-C1-H9	109.65
O5-C1-H8	112.63
O5-C1-H9	104.94
H8-C1-H9	107.16
N1-C2-O3	111.30
N1-C2-H4	110.08
N1-C2-H5	109.70
O3-C2-H4	113.29
O3-C2-H5	105.43
H4-C2-H5	106.80
N1-C3-O1	112.07
N1-C3-H1	110.04
N1-C3-H2	109.59
O1-C3-H1	112.75
O1-C3-H2	104.93
H1-C3-H2	107.20
O2-O1-C3	115.20
O1-O2-H1	108.15
O4-O3-C2	115.24

Table IV-16(continued)

O3-O4-H6	108.48
O6-O5-C1	115.24
O5-O6-H7	107.50
C1-O5-O6-H7	132.81
C2-O3-O4-H6	126.16
C3-O1-O2-H3	128.72

vi. HMTD

The data for HMTD are given in Tables IV-17 through IV-19. The Tables contain, respectively, final atomic parameters, bond lengths, and bond angles.

Table IV-17

Final MNDO Atomic Parameters for HMTD

atom	x	y	z
N1	0.0	0.0	0.0
N2	-0.07723	2.72909	1.57339
C1	1.45606	0.0	0.0
C2	1.32771	3.06365	1.35376
C3	-1.10811	3.35409	0.74801
C4	-0.72368	0.57834	-1.13337
C5	-0.71532	-0.70490	1.05808
C6	-0.49225	2.12852	2.84776
O1	2.01374	1.31331	0.0
O2	2.12672	1.90652	1.13456
O3	-1.61548	2.49429	-0.27091
O4	-0.75042	2.00026	-1.09130
O5	-0.53874	-0.10164	2.33433
O6	-1.24473	0.94136	2.59979
H1	1.84872	-0.44996	-0.95710
H2	1.85542	-0.62588	0.84181
H3	1.78147	3.53531	2.27042
H4	1.43475	3.80200	0.51473
H5	-0.72745	4.31217	0.29689
H6	-2.01779	3.62177	1.35246
H7	-1.75536	0.14230	-1.20706
H8	-0.19767	0.34030	-2.09930
H9	-0.29988	-1.74368	1.18967

Table IV-17 (continued)

atom	x	y	z
H10	-1.80103	-0.81478	0.79568
H11	-1.19727	2.80280	3.40879
H12	0.38527	1.93849	3.51976

Table IV-18

Final MNDO Bond Lengths (Å) for HMTD

N1-C1	1.4561
N1-C4	1.4638
N1-C5	1.4588
N2-C2	1.4608
N2-C3	1.4610
N2-C6	1.4687
C1-O1	1.4268
C1-H1	1.1281
C1-H2	1.1224
C2-O2	1.4232
C2-H3	1.1263
C2-H4	1.1228
C3-O3	1.4265
C3-H5	1.1253
C3-H6	1.1245
C4-O4	1.4228
C4-H7	1.1225
C4-H8	1.1253
C5-O5	1.4226
C5-H9	1.1265
C5-H10	1.1224
C6-O6	1.4273
C6-H11	1.1254
C6-H12	1.1215

Table IV-18 (continued)

01-02	1.2853
03-04	1.2905
05-06	1.2871

Table IV-19

Final MNDO Bond Angles (°) for HMTD

C1-N1-C4	119.63
C1-N1-C5	119.36
C4-N1-C5	120.67
N1-C1-O1	113.01
N1-C1-H1	110.37
N1-C1-H2	110.84
O1-C1-H1	103.36
O1-C1-H2	111.97
H1-C1-H2	106.86
C1-O1-O2	117.34
O1-O2-C2	117.51
O2-C2-N2	112.14
O2-C2-H3	103.87
O2-C2-H4	111.47
N2-C2-H3	111.16
N2-C2-H4	110.77
H3-C2-H4	107.12
C2-N2-C3	119.72
C2-N2-C6	119.73
C3-N2-C6	117.76
N2-C3-O3	113.37
N2-C3-H5	110.61
N2-C3-H6	111.65
O3-C3-H5	110.31

Table IV-19(continued)

O3-C3-H6	103.87
H5-C3-H6	106.65
C3-O3-O4	116.51
O3-O4-C4	114.45
O4-C4-N1	112.41
N1-C4-H7	110.59
N1-C4-H8	110.48
O4-C4-H7	111.89
O4-C4-H8	104.22
H7-C4-H8	106.92
N1-C5-O5	112.64
N1-C5-H9	110.46
N1-C5-H10	110.61
O5-C5-H9	103.91
O5-C5-H10	111.80
H9-C5-H10	107.08
C5-O5-O6	117.42
O5-O6-C6	114.88
N2-C6-O6	109.78
N2-C6-H11	111.38
N2-C6-H12	111.60
O6-C6-H11	104.76
O6-C6-H12	112.07
H11-C6-H12	107.04

Table IV-19 (continued)

C1-O1-O2-C2	113.71
C3-O3-O4-C4	122.03
C5-O5-O6-C6	118.18

vii. Discussion

The data above make some interesting predictions. First of all, one hydroperoxymethyl group is not any more bulky to a central nitrogen atom than is a methyl group, according to MNDO; in fact, it is predicted to be less bulky. The H-N-H bond angle in methylamine was predicted to be 105.59°, whereas the H-N-H angle in hydroperoxymethylamine was predicted to be 106.34°. This immediately suggests that there may be some electronic effects at play. Another indication of electronic effects is the shortening of the average N-H bond length from 1.0084A in methylamine to 1.0073A in hydroperoxymethylamine.

This trend continues in di(hydroperoxymethyl)amine, for which the N-H bond length is predicted to be 1.0062A. The C-N-C bond angle in this compound is predicted to be 123.24°, showing that the hydroperoxymethyl groups do indeed look bulky to each other. The C-N-H bond angles average 112.69°, slightly larger than the 111.95° in hydroperoxymethylamine.

Tri(hydroperoxymethyl)amine shows a dramatic effect: the nitrogen atom is predicted to be almost planar. The average C-N-C bond angle is 119.88°, and the nitrogen atom is a mere 0.05A out of the plane of the carbon atoms. This suggests that the planar configuration is indeed a stable one for nitrogen. Also of interest is the fact that MNDO predicts that each hydroperoxymethyl group points in the same direction relative to the nitrogen atom. It would seem that a conformation in which one group points in a different direction might be less steri-

cally hindered; this again may point to the involvement of electronic effects.

The average C-N-C bond angle predicted for HMTD is 119.48° (the average angles for the two bridgehead nitrogen atoms are 119.89° and 119.07°). The nitrogen atoms are nearly planar; the nitrogen atoms are 0.049Å and 0.142Å out of their respective carbon planes, much closer than the 0.29Å and 0.30Å predicted by MM2. Again, there are indications that electronic effects are involved in this strange geometry. It also seems that the bicyclic structure of HMTD may actually push the nitrogen atoms away from the planar configuration that they seem to favor in tri(hydroperoxymethyl)amine; thus, MNDO also seems to predict some steric interactions.

The structure that MNDO predicts for HMTD is not in full agreement with that observed. MNDO predicts larger N-C and C-O bond lengths, but smaller O-O bond lengths. These differences may be important; in fact, with MNDO might predict planar nitrogen atoms given the observed bond lengths.

One must be careful in interpreting these MNDO results. For instance, it might be that MNDO would incorrectly predict a planar nitrogen atom in all NR_3 compounds for purely steric reasons. Thus, calculations must be done on several NR_3 compounds before any definitive conclusions are drawn from the calculations on HMTD and similar hydroperoxymethyl amines.

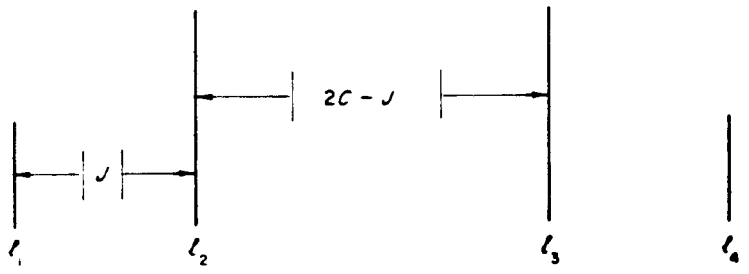
CHAPTER V. NMR

A. Proton NMR

i. Introduction

The experiments described so far have investigated the solid structure of HMTD, for the most part. The dynamic structure of HMTD could be just as interesting as the static structure, however. One interesting question is how fast HMTD changes conformation in solution. The perfect tool for studying this rate is a temperature dependent proton NMR study.

As noted above, the room temperature proton NMR spectrum of HMTD showed an apparent singlet peak. The x-ray structure,



A schematic representation of an AB pattern[43].

Figure V-1

however, indicates that the two geminal protons of the methylene groups ought not to be equivalent, and thus should show what is called an AB pattern in their proton NMR.

An AB pattern arises from two "isolated" interacting nuclei (i.e., nuclei which are not strongly coupled to any other nuclei), denoted by A and B, which are not NMR equivalent but which have similar chemical shifts (if the shifts differed greatly, the pattern would be called an AM or an AX pattern). A full AB pattern has four lines, which I will denote (from left to right) as l_1 through l_4 (see Figure V-1). Lines l_1 and l_4 are of the same intensity. Lines l_2 and l_3 are also of the same intensity; these lines are always more intense than the other two. The separation between lines l_1 and l_2 (and lines l_3 and l_4) is given by the absolute value of the coupling constant, J. It is convenient to define a variable C, such that

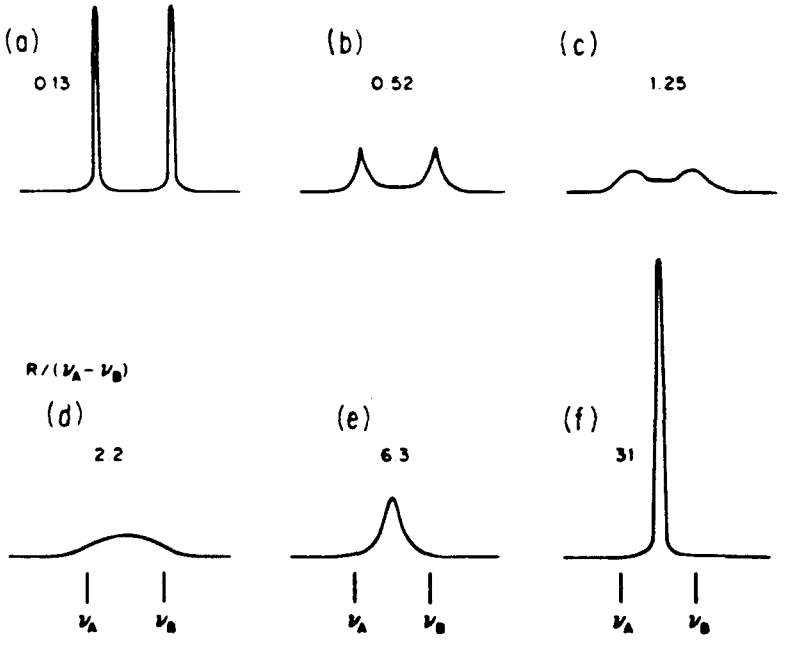
$$2C = [(\nu_A - \nu_B)^2 + J^2]^{1/2}$$

(where ν_A and ν_B are the respective resonance frequencies of nuclei A and B). The separation between lines l_2 and l_3 is then the absolute value of $2C - J$.

The x-ray structure of HMTD suggests that it exists in two enantiomeric forms. A given molecule of HMTD may exchange between these two conformations. Such a chemical exchange can have an effect on an NMR spectrum. Imagine a chemical system which exchanges between two conformations, C and D, where each conformation shows a single, singlet NMR resonance. The rate of this

exchange is R, where $R = 1/2\tau$ (τ is the exchange lifetime). Figure V-2 illustrates this situation for different exchange rates. When exchange is extremely slow or non-existent (a), there are two separate peaks corresponding to each form of the molecule. As the exchange rate increases, the two peaks broaden and begin to coalesce. At an extremely fast exchange rate (f), the spectrum shows one sharp singlet peak.

Since the two exchanging forms of HMTD are enantiomeric, and therefore of the same energy (and thus are equally populated), its proton NMR spectrum should have a rather simple temperature dependence. The ratio of the apparent difference in resonance



Calculated line shapes for various values of the exchange lifetime relative to the difference in frequency of two equally populated sites[43].

Figure V-2

frequencies, $(\nu_A - \nu_B)_{app}$ to the true difference is given by the equation:

$$\frac{(\nu_A - \nu_B)_{app}}{(\nu_A - \nu_B)} = 1 - \frac{1}{2\pi^2 \tau^2 (\nu_A - \nu_B)^2}^{1/2}$$

Thus, τ is a function of $(\nu_A - \nu_B)_{app}$ and $(\nu_A - \nu_B)$. This means that τ, and therefore R, may be derived from an AB pattern, since C is a function of $(\nu_A - \nu_B)_{app}$, the separation between l_2 and l_3 is given by $2C - J$, and J is the the separation between l_1 and l_2. $(\nu_A - \nu_B)$ may be determined from an NMR spectrum taken at a temperature low enough that the chemical exchange process is not observed, and $(\nu_A - \nu_B)_{app}$ may be determined at temperatures at which the exchange is being observed. As the temperature increases, the separation between l_2 and l_3 decreases until they coalesce, but the separation between l_1 and l_2 remains the same; the only effect on l_1 and l_4 is that they lose intensity until coalescence of l_2 and l_3, at which time l_1 and l_4 have disappeared.

Given the exchange rate at various temperatures, one can apply Arrhenius' equation,

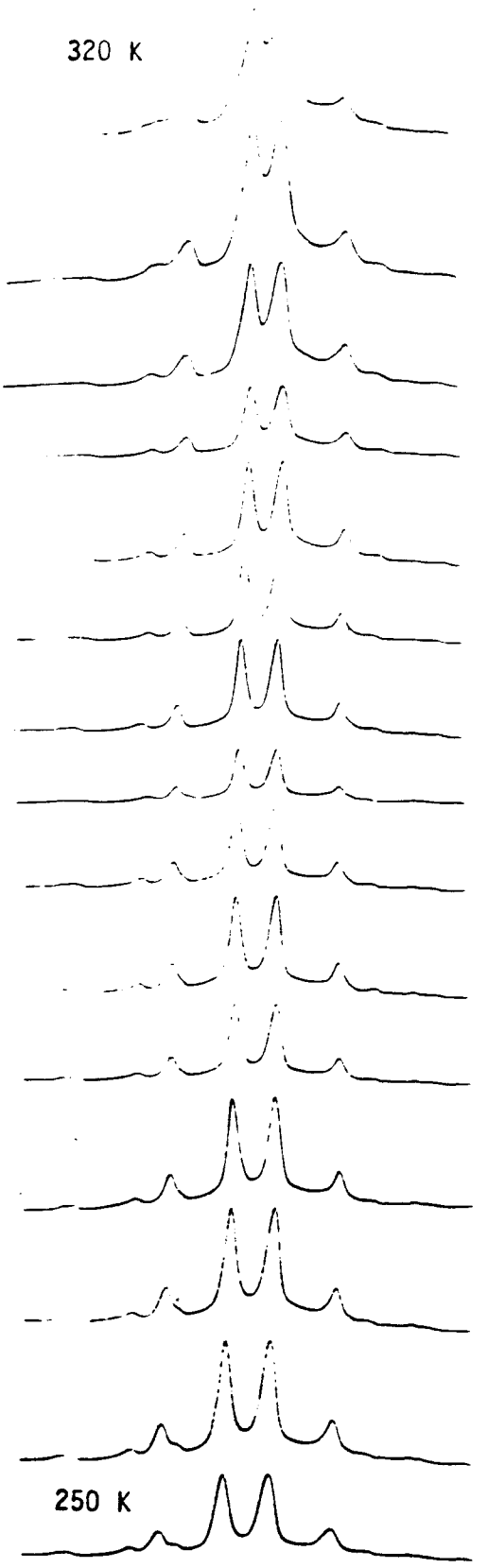
$$\ln(R) = \ln(A) - E_A/RT$$

in order to determine the Arrhenius temperature-independent activation energy, E_A, and the Arrhenius parameter, $\ln(A)$. A graph of $\ln(R)$ vs. $1/T$ will have a slope of $-E_A/R$ and an intercept of $\ln(A)$.

ii. Results and Discussion

Since chloroform freezes at about 210 K and HMTD is about equally soluble in methylene chloride, which freezes at a significantly lower temperature, spectra were run with a saturated solution of freshly recrystallized HMTD in CD_2Cl_2. Spectra were taken every 10° from 200 K to 320 K. These spectra showed an AB pattern at lower temperatures; this pattern was effectively frozen (i.e., there was virtually no exchange taking place) up to 250 K. The temperature was not taken high enough to make the peak coalesce entirely, due to the volatility of methylene chloride.

From this preliminary experiment, it appeared that the region of interest in this solvent was from 250 K to 320 K. Spectra were taken at 5° intervals in this region (Figure V-3). The separation between 1_1 and 1_2 was found to be the same at all temperatures, as expected, giving an absolute value of J of 13.6. An Arrhenius plot was made, and it showed an interesting phenomenon: the rate of exchange has different activation energies at different temperatures (Figure V-4). From 250 K to 270 K, the exchange process has an activation energy of 13.95 kcal/mol and a $\ln(A)$ of 32.06. From 270 K up to 320 K, the activation energy is 4.76 kcal/mol and $\ln(A)$ is 14.99. Since the higher activation energy process is favored at lower temperature, one must conclude that some sort of conformational change takes place at 270 K (in solution). It seems likely that the low temperature conformation is that seen in the crystal structure; the



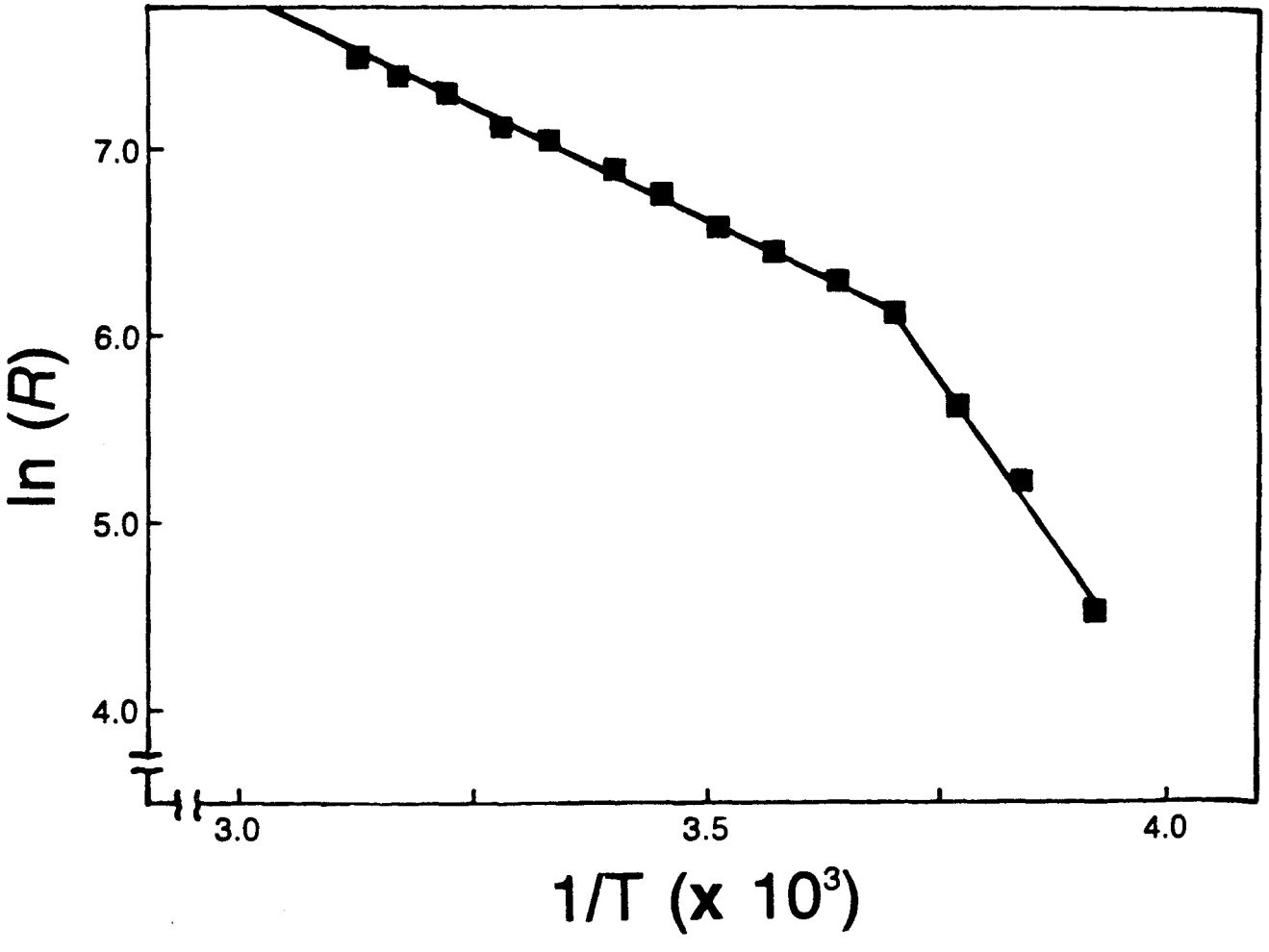
Proton NMR spectra of HMTD in CD_2Cl_2 from 250 K to 320 K.

Figure V-3

Table V-1

Temperature and Rate Data for HMTD

Temperature	2C-J(Hz)	*R* (Hz)	ln(*R*)
250	9.81		
255	9.61	92.17	4.52
260	9.41	183.55	5.21
265	9.21	274.13	5.61
270	8.81	452.93	6.12
275	8.61	541.14	6.29
280	8.41	628.57	6.44
285	8.21	715.20	6.57
290	7.81	886.09	6.79
295	7.61	970.34	6.88
300	7.21	1136.48	7.04
305	6.81	1299.46	7.17
310	6.41	1459.27	7.29
315	6.01	1615.92	7.39
320	5.61	1769.40	7.49



An Arrhenius plot for HMTD from NMR data.

Figure V-4

The exact nature of the high temperature conformation is of great interest. Any large conformational change (which this must be, in order to change the activation energy so much) stands a good chance of having a different nitrogen geometry. The structures of the carbon analog and other molecules of course suggest that if the nitrogen configuration changes, it will probably be to some sort of in,in structure. If this nitrogen puckering is necessary to the exchange process in the first place, the much lower activation energy would be reasonable. Models do suggest that a concerted exchange process may indeed be more sterically favorable with in,in bridgehead nitrogens than with planar ones, although there must be some tradeoff with the unfavorable non-bonded distance between the nitrogen atoms in the in,in conformation. At any rate, some method is needed to study the temperature dependence of the conformation of HMTD rather than simply the exchange rate. ^{14}N NMR was used to investigate just this.

B. ^{14}N Linewidth Studies

i. Introduction

In order to further study the dynamics of HMTD in solution, some method was needed which could monitor the planarity of the bridgehead nitrogen atoms at different temperatures. ^{14}N NMR is the perfect tool for such an experiment, as the ^{14}N linewidth of an HMTD spectrum should be sensitive to the relative planarity of the nitrogen atoms.

Nuclei with $I>1/2$ possess quadrupole moments. These quadrupole moments give rise to energy level splittings in non-spherically symmetrical environments. The separation between these energy levels is proportional to χ, the quadrupole coupling constant, which is expressed as

$$\chi = e^2qQ/h$$

In liquids, rapid reorientations of the molecules or ions average the quadrupole coupling energy to zero. There is an interesting effect related to the quadrupole coupling constant, however, which still allows it to be measured in solution: it is an important relaxation mechanism. In fact, in the extreme narrowing limit, we find that

$$\frac{1}{T_2} = \frac{3}{40}\,\frac{2I+3}{I^2(2I-1)}\,(1+1/3\eta^2)(e^2qQ/\hbar)^2\,\tau_c$$

in which τ_c is the rotational correlation time and $(e^2qQ/\hbar)$ is the coupling constant in Hertz multiplied by 2π. For ^{14}N, in which $I=1$, this formula reduces to:

$$1/T_2 = 3/8\ (1 + 1/3\ \eta^2)(e^2qQ/\hbar)^2\tau_c$$

where η is the asymmetry parameter. This motional narrowing approximation requires that $(e^2qQ/\hbar)\tau_c << 1$. This is indeed true for ^{14}N in almost every case, as the coupling constant is on the order of 10^7 rad sec^{-1} while τ_c is on the order of 10^{-12} sec.[44]

Given this equation, it is simple to find the coupling constant, assuming that the asymmetry parameter is zero (which it is in the case of HMTD, due to its 3-fold symmetry). Since the half-height linewidth under these conditions should be $1/\pi T_2$, the linewidth of an ^{14}N peak at a given temperature should along with a known correlation time should be sufficient to determine the coupling constant. If the correlation time is not known, it may be estimated using the formula

$$\tau_c = 4/3\ \pi\ a^3\ \eta/kT$$

where a is the radius of the molecule in question and η is the solvent viscosity.[45] Thus, a ^{14}N linewidth study of HMTD was undertaken.

ii. Results and Discussion

^{14}N NMR spectra of HMTD were taken in chloroform at three temperatures: 233 K, 273 K, and 313 K. The linewidths at half height were measured in each case. An average radius of HMTD was calculated from the crystal data (radii were measured in the different, representative directions and averaged), and chloroform viscosities at each temperature were found.[46] The results are tabulated in Table V-2. The coupling constants varied from 3.03 MHz at 233 K to 4.14 MHz at 313 K. These numbers are fairly reasonable when compared to those from similar compounds[47]: trimethylamine has a coupling constant of 5.194, triethylamine one of 5.02, ammonia one of 3.161, and ammonia-d_3 one of 3.231. These numbers are suggestive of several things. First of all, the coupling constants for HMTD tend to be small compared to NR_3 coupling constants where R is not hydrogen. Ammonia is known to invert rapidly, however, and so averages into a more closely planar state than might be suggested by its diffraction-derived structure. Ammonia-d_3 is of course harder to invert, and it has a larger coupling constant. On the other hand, the trend seen in trimethyl- and triethyl- amines is that the bulkier the R group (and thus the more planar the nitrogen), the smaller the quadrupole coupling constant. This information fits nicely with the observed coupling constants for HMTD; at low temperature, the bridgehead nitrogen atoms are basically planar, whereas at higher temperatures they have a more puckered configuration. Further-

more, these data correlates well with the proton NMR data. The temperature variation of the ^{14}N coupling constant decreases markedly above 270 K, just as the activation constant for the ring flipping decreases markedly. A ^{14}N coupling constant experiment needs to be done at temperature increments of 5° in order to see how much of a correlation there really is between these processes. I will mention some other possible NMR experiments in the final chapter.

Table V-2

HMTD ^{14}N NMR Linewidth and Coupling Constant Data

T	(cp)	τ_c(sec x 10^{11})	$1/T_2$(Hz)	e^2qQ/h
233	1.13	3.25	117	3.03
273	0.70	1.72	96.9	3.80
313	0.50	1.07	71.8	4.14

CHAPTER VI. SUMMARY AND FUTURE EXPERIMENTS

Since the original crystal structure was done on HMTD, many clues have been obtained which hint at the origins of the strange geometry of the bridgehead nitrogen atoms. No definitive answer has been found, however; many more experiments will be necessary before HMTD and its analogs can be fully understood. Reasonable headway has been made towards answering the three questions posed in Chapter II: (1) Is the unusual geometry of HMTD simply coincidental? (2) What role do steric effects play in this geometry? (3) What role do electronic effects play in this geometry?

The crystal structures of BTDD, CTDD, and HMDD have shown fairly conclusively that the planarity of the bridgehead nitrogen atoms in HMTD is not a coincidence, since the angles between the peroxide-containing bridges was 120° and the nitrogen atoms were nearly planar in each of these compounds. These systems are very crowded, however, and looking at slightly less crowded systems would be a good idea. To investigate a similar series of compounds with three-membered bridges, for instance, the analogous reaction might be performed upon 1,3-diaminopropane, *cis*-1,4-diaminocyclohexane, and 1,8-diaminonaphthalene. These reactions will not be as facile as those for BTDD, CTDD, and HMDD. 1,8-diaminonaphthalene is highly reactive, and in a test synthesis unwanted side reactions seemed to predominate. Furthermore, the desired product in this reaction may also be air sensitive. The reaction with *cis*-1,4-diaminocyclohexane would probably be slow

if it occured at all, since the molecule would probably need to react in the boat conformation to produce the desired product. No solid product was obtained in a test reaction between 1,3-diaminopropane, formaldehyde, and hydrogen peroxide; this may be because the reaction solution was too basic and therefore the hydrogen peroxide was decomposed before it could react; this reaction needs to be run again at neutral pH. A similar reaction could be run with 1,4-diaminobutane. The expected product of this reaction, 1,6-diamino-3,4,8,9-hexaoxabicyclo[4.4.4] tetradecane, is quite similar to HMTD (in that all bridges have four members) and could be quite informative.

The MM2 calculations have shown that some steric effects are indeed involved in determining the geometry of HMTD, but that these are not the only effects at play. The bridgehead nitrogen atoms were predicted to be in a configuration very similar to that found in the carbon analog. The MM2 model might be improved by changing the bond and angle parameters for peroxide groups. The peroxide bond lengths used in this model were on the long side, and shortening them might have a profound effect on the predicted geometry. Making these bonds shorter is likely to force the bridgehead nitrogen atoms closer to each other, an interaction that could be escaped only by moving more towards planarity. This may indeed be a major reason for the disparity between the MM2 and MNDO predictions, since the MNDO peroxide bond lengths were on the short side, if anything. At any rate, another MM2 calculation should should be done using the average peroxide bond length found in other organic peroxides. Further-

more, it would be instructive to do MM2 calculations on the series of hydroperoxymethyl amines studied with MNDO; in fact, all molecules studied with MNDO should also be studied with MM2 in order to better separate the steric and electronic forces at play.

The MNDO calculations have pointed to the involvement of electronic factors in the structure of HMTD. The exact nature of these effects is still not entirely clear, and more calculations need to be done. For instance, calculations on BTDD, CTDD, and HMDD could be helpful (of course, these should be done with MM2 also). As mentioned in the MNDO section, calculations must also be done on various NR_3 compounds to ensure the validity of the calculations that have already been done.

Some of the most interesting results obtained in this study were those concerning the solution dynamics of HMTD. More experiments must be done in this area in order to understand the exact nature of the two observed conformations. First of all, ^{14}N NMR spectra must be taken at five degree intervals in the same region as the proton spectra, as mentioned above. The temperature dependence of the quadruple coupling constant should show a some definite change around the temperature that the Arrhenius plot shows a turning point. Also, HMTD could be synthesized with ^{15}N and ^{13}C in order to study the temperature dependence of the ^{15}N-^{13}C coupling; this could give a good indication as to the geometry of the carbon atoms. It would be interesting to see if there is a change observed in this coupling at the temperature of the conformational change observed with proton

NMR.

There are some other facets of HMTD which merit investigation. For instance, why does HMTD have a large, negative heat of crystallization? A careful look at several unit cells in the HMTD crystal structure might help to provide an answer to this question, and also might help to indicate why HMTD prefers this particular conformation in the solid state (since the NMR evidence suggests that two conformations are possible). It would also be helpful to devise some method of taking a photoelectron spectrum of HMTD (it is difficult to do, since HMTD cannot be sublimated). PES could reveal quite a bit of information about the electronic structure of the bridgehead nitrogen atoms[3]. A neutron crystal structure could be useful, in that the true positions of the hydrogen atoms in HMTD could be found. These positions should be able to give some information about the carbon-nitrogen bonds. Another interesting experiment would be to measure the thermal decomposition rate of HMTD at different temperatures. This experiment could be done conveniently using NMR; samples of HMTD and a reference compound could be placed in heat baths of varying temperatures for a given amount of time. A comparison of the integrated intensities of the HMTD peak and the reference peak would indicate the decomposition rate at that particular temperature. An activation energy for decomposition could be derived from this experiment; this energy might be able to give information about the relative strength of the peroxide bonds, which should be the weakest in the molecule.

Although the experimental results described in this thesis

have provided a great deal of information about HMTD and its analogs, they really only scratch the surface of a complicated problem. Many more experiments, such as those mentioned above, must be performed before a real understanding of HMTD can be achieved.

CHAPTER VII. REFERENCES

1. Legler, L. *Ber.* **1885**, *18*, 3343-3351.

2. Taylor, C.A.;Rinkenbach, W.H. *Army Ordnance* **1924**, *5*, 463-466.

3. Alder, R.W. *Acc. Chem. Res.* **1983**, *16*, 321-327.

4. Cox, J.D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds", Academic Press, London, 1970.

5. Hilderbrandt, R.L.; Wieser, J.D.; Montgomery, L.K. *J. Am. Chem. Soc.*, **1973**, *95*, 8598.

6. Parker, W.; Tranter, R.L.; Watt, C.I.F.; Chang, L.W.K.; Schleyer, P.v.R. *J. Am. Chem. Soc.*, **1974**, *96*, 7121.

7. Park, C.K.; Simmons, H.E. *J. Am. Chem. Soc.*, **1968**, *90*, 2431.

8. Lehn, J.-M. *Acc. Chem. Res.*, **1978**, *11*, 49.

9. Alder, R.W.; Sessions, R.B. *J. Am. Chem. Soc.*, **1979**, *101*, 3651.

10. Alder, R.W.; Casson, A.; Sessions, R.B. *J. Am. Chem. Soc.*, **1979**, *101*, 3652.

11. Alder, R.W.; Orpen, A.G.; Sessions, R.B. *J. Chem. Soc. Chem. Comm.*, **1983**, 999.

12. Alder, R.W.; Moss, R.E.; Sessions, R.B. *J. Chem. Soc. Chem. Comm.*, **1983**, 1000.

13. Davis, T.L. "The Chemistry of Powders and Explosives", Angriff Press, Hollywood, CA, 1943.

14. Schmitz, E. *Ann.*, **1960**, *635*, 73.

15. Ferroni, F.; Ciampelli, G.; Seboli, G. *Proc. 4th Intern. Meet. Mol. Spec.*, **1959**, 2, 762-9.

16. Urbanski, T. paper presented at International Symposium on the Chemistry of Organic Peroxides, Berlin-Adlershof, Sept. 1967.

17. Duchamp, D.J. "CRYM crystallographic computing system" *Am. Crystallog. Assoc. Meet.*, Bozeman, Montana, **1964** Paper B14, 29.

18. "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England. 1974.

19. Groth, P. *Acta Chem. Scand.*, **1964**, *18*, 1301.

20. Groth, P. *Acta Chem. Scand.*, **1964**, *18*, 1801.

21. Groth, P. *Acta Chem. Scand.*, **1965**, *19*, 1497.

22. Groth, P. *Acta Chem. Scand.*, **1967**, *21*, 2608.

23. Groth, P. *Acta Chem. Scand.*, **1967**, *21*, 2631.

24. Groth, P. *Acta Chem. Scand.*, **1967**, *21*, 2695.

25. Groth, P. *Acta Chem. Scand.*, **1967**, *21*, 2711.

26. Groth, P. *Acta Chem. Scand.*, **1969**, *23*, 1311.

27. Groth, P. *Acta Chem. Scand.*, **1969**, *23*, 2277.

28. Groth, P. *Acta CHem. Scand.*, **1975**, *29*, 783.

29. Schulz, F. *Ber.*, **1967**, *100*, 2242.

30. Gimarc, B.M. *J. Am. Chem. Soc.*, **1970**, *92*, 266-275.

31. Hunt, R.H.; Leacock, R.A.; Peters, C.W.; Hecht, K.T. *J. Chem. Phys.*, **1965**, *42*, 1931-1946.

32. Johnson, C.K. ORTEP Report ORNL-5138, Oak Ridge National Laboratory, TN, 1965.

33. Allen, P. W.; Sutton, L.E. *Acta Cryst.*, **1950**, 3, 46 (per V.

Schomaker).

34. Newkome, G.R.; Majestic, V.; Fronczek, F.R.; Atwood, J.L. *J. Am. Chem. Soc.*, **1979**, *101*, 1047-1048.

35. Whittleton, S.N.; Seiler, P.; Dunitz, J.D. *Helv. Chim. Acta*, **1981**, *64*, 2614-2616.

36. Gimarc, B.M. *J. Am. Chem. Soc.*, **1974**, *93*, 593-599.

37. Deb, B.M. *J. Am. Chem. Soc.*, **1974**, *96*, 2030-2044.

38. Von Girsewald, C.; Siegens, H. *Ber.*, **1921**, , 492-498.

39. Main, P.; Hull, S.E.; Lessinger, L.; Germain, G.; Declercq, J-P; Woolfson, M.M. MULTAN-78. University of York, York, England. 1978.

40. Allinger, N.L.; Yuhy, Y. *QCPE*, **12**, *1980*, 395.

41. Burkert, U.; Allinger, N.L. "Molecular Mechanics", American Chemical Society, Washington, D.C., 1982.

42. Dewar, M.J.S.; Thiel, W. *J. Am. Chem. Soc.*, **1977**, **99**, 4899, 4907.

43. Becker, E.D. "High Resolution NMR Spectroscopy--Theory and

Chemical Applications" Academic Press, Orlando, FL. 1980.

44. Moniz, W.B.; Gutowsky, H.S. *J. Chem. Phys.* **1963**, 38, 1155.

45. Burke, T.E.; Chan, S.I. *J. Mag. Res.*, 1970, 3, 55.

46. "Perry's Chemical Engineer's Handbook" 50 ed., McGraw-Hill, NY 1984.

47. Lehn, J.M.; Kintzinger, J.P. from "Nuclear Quadrupole Coupling Constants", Academic Press, NY, 1969.